

INVESTIGATION OF
BATTERY ACTIVE NICKEL OXIDES

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ABSTRACT

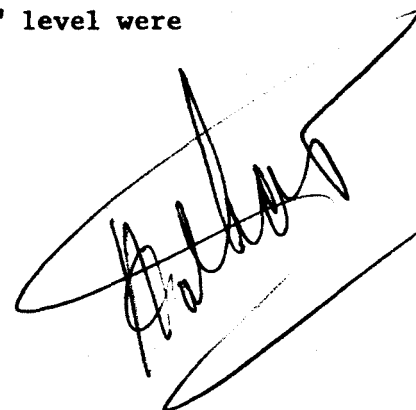
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The study of the effect of stand, at various temperatures, on the tubular graphitic nickel oxide electrode was concluded. With this, Phase I was brought to an end.

The investigation into the effect of overcharge on the composition of the sintered nickel oxide electrode was continued. The positive electrode of a two plate cell was continually monitored by X-ray equipment during charge, overcharge and stand. Diffraction patterns were taken between the angles of $2\theta = 12^\circ$ to 14.5° . The growth during charge and overcharge, and the decline on stand, of a peak between these two angles were noted. In a separate experiment, it was shown that no "strange" lines occurred because of crystallization of KOH during overcharge.

The study concerned with the effect of state-of-charge on the composition of sintered plate nickel oxide electrodes was continued. The study was made by means of X-ray diffraction patterns obtained from positive electrodes charged and discharged to various degrees at the C and C/10 rates. The analysis of positive electrodes at various states of charge, by means of differential thermal analysis and chemical analysis has been started.

Positive electrodes discharged to the "graphitic" level were also analyzed by means of X-ray and D.T.A.

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I. INTRODUCTION

A. PURPOSE

Work performed under this contract is directed (1) toward an identification of the nickel oxide compounds formed during charge and discharge of the electrodes; (2) to determine when they are formed; (3) to determine which factors (such as current density and temperature) affect the charge process; (4) to relate the shelf loss process to these compounds, and (5) to determine the compounds which disappear during discharge of these electrodes.

In order to accomplish this, a three phase program has been devised.

Phase I is directed toward a study of shelf life changes in the nickel electrode at room temperature and certain low and elevated temperatures.

Phase II deals with the forms of nickel oxides appearing at various states of charge, and also with the appearance of unstable oxides during dynamic overcharge.

Phase III deals with methods to prepare positive sintered plate electrodes which are stable at high temperatures with respect to shelf and cycle life.

B. MEETINGS

On January 5, 1965 a meeting was held with Mr. W. Nagel of Nasa Lewis; Mr. P. Ritterman, Drs. R. C. Shair and H. N. Seiger represented Gulton Industries. The meeting took place at Gulton Industries, Metuchen, New Jersey. It was decided to continue work as had been planned.

II. OUTLINE OF PROGRAM

The three phase program which has been described in the First and Second Quarterly Reports deals with the following:

A. PHASE I

The effect of stand on the chemical, electrochemical and structural characteristics of the sintered nickel and tubular graphite nickel electrode was investigated. These characteristics have been studied by X-ray diffraction, chemical analysis, differential thermal analysis, and spectrograph.

B. PHASE II

The oxides of nickel formed during overcharge have been studied. Since these oxides are unstable, it was necessary to study them during continuous overcharge by means of X-ray diffraction patterns. The appearance, growth, shift, and ultimate disappearance of lines not associated with stable nickel oxides and nickel have been followed.

The effect of state of charge and rate of charge on the structural chemical and electrochemical characteristics of sintered nickel electrodes were studied. The same will be done for tubular electrodes.

C. PHASE III

The stabilization of nickel compounds formed during charge and overcharge in a nickel electrode will be attempted, especially for high temperature use. Electrodes will be evaluated for their performance at elevated temperatures up to 70°C. This evaluation involves testing of electrodes individually and as part of cells. The details of these test procedures have been fully discussed in the first two Quarterly Reports.

III. EXPERIMENTAL PROCEDURES & RESULTS

A. EXPERIMENTAL PROCEDURES

1. Phase I

The procedures involving construction, forming, cycling, and characterization of tubular and sintered nickel electrodes have been reported and discussed in detail in the First and Second Quarterly Reports.

The study of the effect of prolonged stand at various temperatures of tubular nickel electrodes was completed during this quarter. Cells 8, 2, and 24 which had been three months on stand at 10°C, 25°C, and 50°C were opened and the positive material X-rayed.

2. Phase II

(a) Unstable Nickel Oxides

A two plate cell having a positive electrode 1 x 2 x 0.09 cm., and a negative electrode of the same thickness but twice the area, were contained within a polyethylene bag. The positives and negatives had tabs extending through the bag. This made it possible to charge the cell. The positive of this cell was X-rayed during charge, overcharge, and open circuit, as was described in the Second Quarterly Report. The discharged cell was placed on charge at 50 ma within the goniometer of the X-ray apparatus and continually monitored between an angle sweep of $2\theta = 12^\circ$ to 14.5° . The cell was swept between $2\theta = 12^\circ$ to 14.5° , also, while on opened circuit for an additional 4 hours. After 65 hours on open circuit, another series of sweeps were made between $2\theta = 12^\circ$ to 19° . The cell was

discharged, and again charged in the goniometer at 50 ma. The sweep was increased to $2\Theta = 10^\circ$ to 80° . The charge continued for $2\frac{1}{2}$ hours. The cell was then swept between $2\Theta = 10^\circ$ to 80° on opened circuit initially, and after 16 hours.

In order to show that no "strange" lines occur due to the precipitation of KOH crystals, a cell consisting of two unimpregnated sintered plates was built and charged in the goniometer in the same manner. The cell was charged for 4 hours at 200 ma.

(b) Stable Nickel Oxides

After formation cycles of the standard 3 negative, 2 positive plate cells, as described in the Second Quarterly Report, were completed, it was necessary to determine the C and C/10 rates for these cells.

The capacity at the C and C/10 rate was determined by discharging three cells at the theoretical C and C/10 rate. The theoretical is defined as the coulombic equivalent of the mean number of moles of nickel hydroxide gained by the sintered material during impregnation. The theoretical rates, on this basis, are C = 1.5 amperes, C/10 = 0.150 amperes.

(1) Determination of C and C/10 rates.

i. C Rate

Three cells (1, 9, and 10) whose capacity on the 5th formation discharge was approximately equal (see Table III of the 2nd Quarterly Report), were charged at 0.75 amperes for a period of 2 hours and 45 minutes and then at 0.50 amperes for an additional 65 minutes. The cells were then discharged at 1.5 amperes.

ii. C/10 Rate

Three additional cells, 8, 4, and 27 of the 36 formed (Table III, 2nd Quarterly Report) were charged for a period of 20 hours at 0.150 ampere and then discharged at the same rate.

(2) State of Charge Tests

i. C Rate

Charge to 200% of Capacity

Cells 1, 9, and 10 were charged at the C rate for a period of two hours. The cells were allowed to stand on open circuit for 24 hours, at which time their positive plates were X-rayed. One of the positive plates of cell 1 was also X-rayed after a 72 hour stand.

Charged 10% Beyond Vigorous Gassing

Cell 5 was rebuilt to allow positive to be visible by the removal of the shims. The cell was charged at the C rate. After vigorous gassing was noticed from the positive, the charge was continued an additional 10% of the input necessary to start the gassing. After a 24 hour stand, the positive plate of this cell was X-rayed.

Charged 20% Below Vigorous Gassing Point

Cells 19 and 24 were charged at the C rate for a length of time 20% less than that required to achieve vigorous gassing, as had been determined previously. The positive of cell 19 was X-rayed following a 24 hour stand. The positive of cell 24 was X-rayed after a 72 hour stand.

Charged 200% - Discharged 50%

Cells 23 and 32 were charged at the C rate for two hours and then immediately discharged at the same rate for 30 minutes. The positive of cell 32 was X-rayed following a 24 hour stand. The positive of cell 23 was X-rayed following a 72 hour stand.

Charged 200% - Discharged 75%

Cell 25 was charged at the C rate for 2 hours after which it was discharged for 45 minutes at the same rate. Following a 72 hour stand, the positive of the cell was X-rayed.

Charged 200% - Discharged to Cell Voltage of Zero

Cell 28 was charged at the C rate for 2 hours and then discharged at the same rate to a cell voltage of zero. After a 72 hour stand, the positive of the cell was X-rayed.

ii. C/10 RateCharged 200% of Capacity

Cells 13, 16, and 18 were charged at the C/10 rate for 20 hours. A positive plate of each of the cells was X-rayed following a 72 hour stand.

Charged 10% Beyond Vigorous Gassing

Cell 7 was rebuilt in such a manner as to make vigorous gassing from the positive visible (the shims were removed).

The cell was charged at the C/10 rate to a coulombic input 10% in excess of that necessary to produce vigorous gassing. After a 72 hour stand, the positive of the cell was X-rayed.

The test was repeated using cell 30, which was charged at the C/10 rate for 11 hours. After a 24 hour stand, an X-ray was made of one of its positive plates.
Charged 20% Below Vigorous Gassing Point.

Cells 17 and 26 were charged at C/10 to an input equal to 20% less than that required to produce vigorous gassing. After a 48 hour stand, an X-ray was taken for the positives of both cells. The test was repeated with cell 31 by charging it for 8 hours at the C/10 rate. After a 24 hour stand, its positive was X-rayed.

Charged 200% - Discharged 50%

Cell 4 was charged 20 hours at the C/10 rate and then discharged at the same rate for 5 hours. The cell was on open circuit stand for 72 hours before its positive was X-rayed.

Charged 200% - Discharged 75%

Cell 22 was charged for 20 hours at the C/10 rate and then discharged at that rate for 7.5 hours. Following a 72 hour stand, the positive of the cell was X-rayed.
Charged 200% - Discharged to Cell Voltage Equals Zero

Cell 36 was discharged to a voltage of $V = 0$ at the C/10 rate after it had received a 20 hour charge at that rate. This, too, was a positive capacity limited

cell. After a 72 hour stand, the positive was subjected to analysis by X-ray.

3. Development and Improvement of Measuring Techniques

(a) Differential Thermal Analysis

Three thin chromel-alumel thermocouples were mounted into a new stainless steel block. One thermocouple in the block records ambient temperature. The other two are set with polarity in opposition to each other to record the temperature difference between the sample and the alumina standard. The X-Y recorder is used to automatically plot temperature differences between ambient and the temperature differential existing between alumina and sample. Three holes in the block hold the three thermocouples. The thermocouple measuring ambient temperature is cemented into the hole. The sample is powdered and a weighed quantity packed into the sample compartment. The following samples were investigated by differential analysis:

Alumina, Ni(OH)_2 prepared in July 1964 and used for graphite plates; Ni(OH)_2 more recently prepared; commercial Ni(OH)_2 obtained from McKay and Company; charged sintered plates; sintered plates discharged to the "graphitic" level; completely discharged sintered plates (below the "graphitic" level); and $\text{Ba(NO}_3)_2$.

(b) Chemical Analysis

(1) Nickel

The determination of nickel has been done by precipitation from basic solution, as nickel dimethylglyoxime. The method has been checked using pure nickel. Determinations have been made on a purchase sample of nickel hydroxide, and on the nickel hydroxide graphite mix used in the preparation of tubular plates.

(2) Oxygen

The determination of oxygen was done by means of reacting a sample with an excess of an acid solution of potassium iodine and titration of the liberated iodine with sodium thiosulfate.

Determinations were made on $\text{Ni}(\text{OH})_2$ (prepared in July 1964), a charged sintered positive plate (charged at C/10), a discharged positive plate and a charged plate (charged at the C rate).

(3) Hydrogen

The apparatus for the determination of hydrogen has been set up and is shown in Figure 1.

Hydrogen is determined by oxidizing the sample with K_2CrO_4 and PbCrO_4 at 600°C . The reaction occurs in a porcelain boat. A hot air blower forces the oxidized hydrogen (steam) into a weighed drying tube.

(4) Determination of Average Valence State of Nickel Compounds

The washed and dried sample was dissolved in an excess acidic As_2O_3 . After the dissolution, the remaining As_2O_3 was determined by titration with standard KMnO_4 . A determination of nickel by precipitation with dimethylglyoxime completes the analysis. This determination has been made on a charged sintered nickel plate and a charged pocket plate.

4. Special Tests - Analysis of Sintered Nickel Electrodes at the Graphitic Level

(a) By Means of X-ray Diffraction

Cells 3, 33, and 34 from Phase II (see Table III of the Second

Quarterly Report) were charged at the C/10 rate for 18 hours and discharged to a cell voltage of zero at 500 ma. The cells were placed on dead short for 4 hours and again charged at the C/10 rate for 17 hours. They were discharged to 0.0 volts at 0.30 amps with the voltage traced by means of a recorder. The shorting and charge were repeated. The cells were then discharged to the beginning of the "graphitic" level and then allowed to stand on open circuit for 24 hours before a positive of each cell was analyzed by means of X-ray diffraction.

(b) By Means of Differential Thermal Analysis

The positives of cells 3 and 33 were washed with distilled water and air dried. Samples from each plate were ground in a mortar and pestle and stored in the sample holder of the stainless steel block. Both samples were then analyzed by differential thermal analysis as has been described in this report.

B. DATA

1. Phase I

The X-ray diffraction patterns obtained from the positives of tubular cells 8, 2, and 24 appear in Figures 2, 3 and 4 respectively. Cells 8, 2 and 24 had been on three month stand at 10°, 25° and 50°C.

All other data generated for Phase I have been presented in the First and Second Quarterly Reports.

2. Phase II

(a) Unstable Nickel Oxides

Figure 5 shows the change in intensity of the X-ray diffraction pattern between $2\theta = 12^\circ$ to 14.5° with charge time and on opened circuit. A peak appears at 13.7° growing during charge and decaying on opened circuit. After 65 hours, the peak at 13.7 has disappeared. Figure 6 shows the X-ray diffraction patterns of the positive between $2\theta = 10^\circ$ to 80° while the cell was being charged at 50 ma (the C rate).

Figure 7 shows the sweep for $2\Theta = 80^\circ$ to 10° with charge continuing. At the completion of this sweep, the cell had been on charge 140 minutes. Figure 8 shows a sweep between $2\Theta = 80^\circ$ to 10° with the cell on open circuit. Figure 9 shows a sweep between $2\Theta = 10^\circ$ to 80° after the cell has been on opened circuit for 16 hours. Fig. 10 shows a sweep between $2\Theta = 10^\circ$ to 80° of a sintered plate being positively charged at 200 ma. Fig. 11 shows the same sweep after the cell had been on continuous charge for 4 hours.

(b) Stable Nickel Oxides

(1) Determination of the C and C/10 Rate

i. C Rate

Cells 1, 9, and 10 when discharged at 1.5 amperes required 46 minutes to reach 0.0 volts. To the nearest tenth, the C rate then was set equal to 1.2 amperes.

ii. C/10 Rate

Cells 8, 4 and 27 when discharged to 0.6 V at 0.150 amperes required 9 hours and 56 minutes, 10 hours and 4 minutes, and 9 hours and 48 minutes respectively. Thus, 0.150 ampere was established as the C/10 discharge rate.

(2) State of Charge Tests

i. C Rate

Charged 200% of Capacity

The positives of cells 1, 9, and 10 yielded X-ray patterns which were a duplicate of one another. Fig. 12 showing X-ray patterns of a positive of cell 1 is typical. The other positive of the cell was X-rayed following a 72 hour stand. The pattern is shown in Figure 13.

Charged 10% Beyond Vigorous Gassing Point.

The positives of cell 5 began to gas vigorously after being on charge for 65 minutes at 1.2 amperes. The

cell was continued on charge for a total of 71.5 minutes. Figure 14 shows the X-ray pattern obtained from a positive plate of cell 5.

Charged 20% Below Vigorous Gassing Point

Cells 19 and 24 were charged at 1.2 amperes for 52 minutes which corresponds to 20% less input than required to reach vigorous gassing. The pattern obtained from the positive of cell 19 is shown in Fig. 15.

Charged 200% - Discharged 50%

X-ray patterns were obtained from the positives of cells 23 and 32. Figure 16 shows the typical result. It is the X-ray pattern of cell 23. Previous to X-ray the cells were charged for 2 hours at 1.2 amperes and discharged for 30 minutes at the same rate.

Charged 200% - Discharged 75%

Cell 25 was charged at 1.2 amperes for 2 hours and then discharged for 45 minutes at the same rate. The X-ray pattern obtained from the positive of this cell is shown in Fig. 17.

Charged 200% - Discharged to Cell Voltage of Zero

Cell 28 was charged at 1.2 amperes for 2 hours and then discharged to a cell voltage of zero, at the same rate. The cell required 55 minutes of discharge to reach zero volts. The X-ray diffraction pattern of a positive of this cell is shown in Fig. 18.

ii. C/10 Rate

Charged 200% of Capacity

The X-ray patterns appearing in Figure 19 is typical for the positives of cells 13, 16 and 18. These cells were charged at 0.150 amperes, which was the value determined as the C/10 rate.

Charged 10% Beyond Vigorous Gassing Point

Cell 7 required a charge of 855 minutes at 0.150 amperes before vigorous gassing was noticed. The cell received an additional 85 minutes of charge. The X-ray diffraction pattern from a positive of this cell is shown in Figure 20.

Cell 30 was charged at 0.150 amperes for 11 hours and its positive was X-rayed. The pattern obtained is shown in Figure 21.

Charged 20% Below Vigorous Gassing Point

The X-ray diffraction pattern of cells 17 and 26 were observed and found similar to each other. The pattern obtained for the positive of cell 17 is shown in Figure 22. Previous to X-ray, these cells were charged 684 minutes at 0.150 amperes, which corresponds to an input of 20% below that required to reach vigorous gassing.

The X-ray pattern of a positive of cell 31 appears in Figure 23. This cell was previously charged for 8 hours at 0.150 amperes.

Charged 200% - Discharged 50%

Cell 4 was charged at 0.150 amperes for 20 hours and then discharged at that rate for 5 hours. Its positive was X-rayed and the pattern obtained appears in Figure 24.

Charged 200% - Discharged 75%

The X-ray pattern obtained from the positive of cell 22 is shown in Figure 25. The cell was previously charged for 20 hours at 0.150 amperes and then discharged for $7\frac{1}{2}$ hours at 0.150 amperes.

Charged 200% - Discharged to Cell Voltage of Zero

Cell 36 was charged at 0.150 amperes for 20 hours and then discharged to a cell voltage of zero. The discharge required 11 hours and 42 minutes. The X-ray pattern obtained from a positive of this cell appears in Figure 26.

3. Development and Improvement of Measuring Techniques

(a) Differential Thermal Analysis

D. T. A. calibration with alumina and $\text{Ba}(\text{NO}_3)_2$ yielded satisfactory data. Three samples of $\text{Ni}(\text{OH})_2$, two of which were prepared in this laboratory, one of which was purchased, were analyzed. The results indicated a transition at temperatures of 539°F , 580°F and 660°F for the samples prepared here in July 1964 and in early 1965, and for the purchased sample. A thermogram obtained from a sintered nickel plate, charged at the C rate, appears in Figure 27. Various phase changes are indicated. Figure 28 shows a thermogram for a sintered positive charged at C/10. An even greater number of transitions are indicated here. A thermogram of a completely discharged plate,

Figure 29, indicates only one transition at 583°F . Figure 30 is a thermogram of a sample of a positive plate discharged to the "graphitic" level. This differs from that obtained with the charged and completely discharged plates.

(b) Chemical Analysis

(1) Nickel

The standardization showed the dimethylgloxime method for nickel to be highly accurate and precise. The amount of nickel found in the $\text{Ni}(\text{OH})_2$ which was used for the tubular plates corresponded to the theoretical amount. The sample received from an outside source contained only 95% of the expected amount of nickel.

(2) Oxygen

No oxygen was found by this method for $\text{Ni}(\text{OH})_2$ or in the discharged plate. Less than 5% of the expected amount was found for the charged plate.

(3) Hydrogen

The apparatus for the determination of hydrogen has been set up. Data will be obtained during the next quarter.

(4) Determination of Average Valence State of Nickel Compounds

It was found necessary to perform the titration of excess As_2O_3 with KMnO_4 at a temperature of 90°C in order to make it proceed with sufficient rapidity. As yet, we do not have sufficient data to report the valence state of nickel by this method.

4. Special Tests - Analysis of Sintered Nickel Electrode at the Graphitic Level

(a) By Means of X-ray

No major difference between the main peaks of a completely discharged plate and those at the graphitic level are apparent.

(b) By Means of Differential Thermal Analysis

Figure 30 shows a thermogram of the positive plate of a cell discharged to the graphitic level. This thermogram is considerable different from that obtained from a completely discharged positive. The thermogram indicates several transitions for a plate discharged to the graphitic level, while, as previously mentioned, only a single change is indicated by the completely discharged plate.

C. DISCUSSION

1. Phase I

The "d" spacings obtained from tubular plate materials after storage for 3 months at 10⁰, 25⁰, and 50⁰C were tabulated and compared to similar plate material after storage for 24 hours at the same three temperatures. The 24 hour data were given in Figures 8, 7, and 9 of the Second Quarterly Report. The intensity of these spacings are shown in Table I. (The intensity is the difference between peak height and background level). The table reveals the formation of additional spacings after extended stand, especially for the material kept at 50⁰C. The decrease in intensity of "d" = 2.32 to 2.34⁰A after extended storage would indicate that in a tubular electrode this line is associated with a form of nickel oxide which undergoes change during stand.

2. Phase II

(a) Unstable Nickel Oxides

The peaks corresponding to the "d" spacings have been tabulated for the positive of the cell while it was on charge and overcharge. This was also done for initial opened circuit and after 16 hours on opened circuit. As Table II shows, a peak occurs at "d" = 6.95 ($2\theta = 12.7^\circ$) which is formed during charge and overcharge and which decays during stand. It has completely decayed after 16 hours of stand. This peak is, most probably, the same one encountered during the continuous sweep of $2\theta = 12^\circ$ to 14.5° (Figure 5). According to Toumi's recent article, a tetravalent phase of nickel is associated with $2\theta = 125^\circ$. This peak value has also been associated with γ NiOOH.

Figures 10 and 11, for the sintered Ni being anodized, show peaks at "d" = 4.47-4.53 and 2.47 in addition to the nickel and polyethylene peaks. These two peaks did not increase in intensity after a 4 hour charge and are associated with Ni(OH)_2 . Thus, it can be concluded that no "strange" peaks occur due to the drying out of KOH on overcharge.

(b) Stable Nickel Oxides

The "d" spacings and their intensities at various states of charge are shown in Table III. This has been done for both the C and C/10 rates. Due to the discrepancy between gassing point and capacity at the C/10 rate, additional tests were run, taking 10 hours as full charge and charging 10% above and 20% below this value (Figure 21, 23).

All the positive electrodes showed a peak for $d = 4.50$ to 4.70\AA . The intensities at this "d" value seemed the same for all plates charged and discharged at the C rate (Figs. 12 through 18). The two plates considerably overcharged at the C/10 rate (Fig. 19 and 20) also exhibited an intensity similar to the plates charged and discharged at the C rate. The intensities for the remaining plates charged and discharged at the C/10 rate (Figs. 20-26) are less than half the magnitude of those described in the two previous sentences. The literature dealing with X-ray studies of nickel oxide electrodes has ascribed $d = 4.50$ - 4.70\AA to both the charged and discharged state. No significance can yet be assigned to these data.

Peaks appear at all states of charge for $d = 2.47\text{\AA}$ except one. The plate completely discharged at the C/10 rate (Fig. 26) is the exception. The plate completely discharged at the C rate (Fig. 18) has the lowest intensity for this "d" spacing. Since the plate discharged completely at the C/10 rate was driven to a lower state of charge than that discharged at the C rate (due to overvoltage and I.R. drop), the low value shown in Fig. 18 and the complete disappearance of the peak in Fig. 26 is significant. The intensities obtained at this "d" value show no significant variation among the other plates (Figs. 12-17, 19-25). It is concluded, therefore, that the peak of $d = 2.47\text{\AA}$ is associated with a dischargeable nickel oxide. When only Ni(OH)_2 is present, the line is completely missing.

The peak appearing at $d = 3.73$ - 3.77\AA shown in Table III, and those at $d = 3.62$ - 3.73\AA in Table II, can be assumed to be the same. These peaks appear during charge and overcharge and do not decay

on stand (Table II). At the C rate charge and discharge (1.2 amps) this line appears in all plates, Figures 12-17, except the plate completely discharged, Figure 18, (Table III).

At the value $d = 2.32\text{-}2.36\text{\AA}$ ⁰ no line appears for the four plates which were considerably overcharged and not discharged, (Figures 12, 13, 19 and 20). This line appears for all the other plates. This indicates that the peak at $d = 2.32\text{-}2.36\text{\AA}$ ⁰ is associated with the discharged state of the nickel electrode. Its absence as a peak among those given in Table II supports the above contention.

In order to quantitatively determine the state-of-charge of the nickel oxide electrode by means of X-ray diffraction, it may be necessary to consider the depth of penetration of X-rays into the sintered plate electrode. The diffraction patterns obtained from a plate which has been discharged 50% appear the same as those obtained from a plate discharged 75%.

The formation of nickel compounds during charge and discharge of the sintered plate electrode can occur by one of the two following mechanisms; (1) atom transfer at the electrolyte/active material interface with charge transfer at the active material/grid interface; (2) both charge and atom transfer at the electrolyte/active material interface. The data would indicate that the first mechanism correctly describes the processes occurring during charge and discharge of the sintered plate positive electrode.

3. Development and Improvement of Measuring Technique

(a) Differential Analysis

The single transition which was found to occur corresponds to that found for the completely discharged plate (Fig. 29). This would indicate that the active material of completely discharged plates consists essentially of Ni(OH)_2 . The plate charged at the C rate indicates the presence of some Ni(OH)_2 as well as other compounds (Fig. 27). The plate charged at the C/10 rate indicates even a greater number of compounds than that charged at the C rate. (Fig 28) The plate discharged to the "graphitic" level indicates compounds different from both the charged and discharged plates, as seen in Fig. 30. These compounds remain to be identified.

(b) Chemical Analysis

(1) Nickel

The fact that the amount of nickel determined from the purchased Ni(OH)_2 was only 95% of the theoretical value indicates the presence of some impurity.

(2) Oxygen

The method using KI and sodium thiosulfate for the determination of oxygen is not satisfactory for our purpose. An alternate method, involving decomposition of the sample and the subsequent absorption of oxygen, will be utilized henceforth.

4. Special Tests - Analysis of Sintered Nickel Electrode at the "Graphitic" Level.

X-ray diffraction indicated no difference between the positive plates discharged to the "graphitic" level and those completely discharged, however, D.T.A. indicated considerable differences. The compounds

corresponding to the "graphitic" level, found by means of D.T.A., may either be adjacent to the grid or amorphous. Either of these considerations would mask their appearance when analyzing by means of X-ray.

D. CONCLUSIONS

1. A nickel oxide compound is formed during charge and overcharge of the positive electrode which has a peak between $2\theta = 12^\circ$ and 14° . The peak has been associated with a tetravalent nickel compound in Toumi's recent article. It has also been associated with γ NiOOH. The peak grows during charge and decays during stand. It disappears completely after 16 hours opened circuit stand.
2. Compounds other than Ni(OH)_2 exist at the "graphitic" level. This has been found using D.T.A., but is not visible by means of X-ray diffraction.
3. The hypothesis that "d" lines are formed during extended overcharge due to crystallization of KOH has been disproved.
4. The line $d = 2.47\text{\AA}$ obtained by X-ray diffraction of a positive electrode is associated with a dischargeable nickel oxide. According to the ASTM files, this line can be associated with β NiOOH, γ NiOOH, $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and $\text{Ni}_3\text{O}_2(\text{OH})_4$.
5. The line $d = 2.32\text{--}2.36\text{\AA}$ is associated with a discharged nickel oxide. ASTM files associate this line with Ni(OH)_2 .

IV WORK PLANNED FOR THE NEXT QUARTER

A. CONTINUATION OF OVERCHARGE EXPERIMENT

The half-life of the compound corresponding to $d = 6.95\overset{0}{\text{\AA}}$ will be determined. An attempt will be made to determine the valence state of the nickel in this compound.

B. CHEMICAL ANALYSIS

1. Hydrogen

The hydrogen analysis, as described in the text of this report and as shown in Fig. 1, will be performed on the nickel electrode.

2. Oxygen

The determination of oxygen by means of the acidic KI method has been abandoned, and in its stead, we will use Oxorbent to absorb oxygen from a thermally decomposed sample.

3. Valence State of Nickel

The determination of the valence state of nickel in plates at various states of charge, by the means outlined in this report, will be continued.

4. Formula Weight

Formula weights corresponding to the charged and discharged state of the active material of a nickel electrode will be determined.

C. D.T.A.

Electrodes at various states of charge will be analyzed under reducing and inert atmospheres.

D. PHASE III

The preparation of electrodes capable of retaining charge at elevated temperatures will be initiated. These will be tested, as was described in the outline of the program in the First and Second Quarterly Reports.

V. REFERENCES

- 1 Investigation of Battery Active Nickel Oxides
First Quarterly Report, P. Ritterman and H. N. Seiger.
- 2 Investigation of Battery Active Nickel Oxides
Second Quarterly Report, P. Ritterman and H. N. Seiger.
- 3 The Forming Process in Nickel Positive Electrodes,
D. Toumi, Journal of the Electrochemical Society,
Jan. 1965.
- 4 A.S.T.M. Files

TABLE I

INTENSITIES OF "d" SPACINGS
OBTAINED FROM ACTIVE MATERIAL OF
TUBULAR POSITIVE ELECTRODE*

FIGURE	STORAGE TEMP.	TIME ON O.C. †	"d" SPACINGS							
			4.49-4.61	3.59-3.68	2.99	2.61-2.68	2.32-2.34	2.29-2.28	2.25	1.47
2	10°	3 Months	9	5	---	4	---	6	---	---
3	25°	3 Months	10	5	---	5	10	---	---	---
4	50°	3 Months	7	12	9	8	10	8	5	---
(Figs. 7, 8, and 9 -- See Second Quarterly Report)										
(8)	10°	24 Hours	11	6	---	8	38	---	---	4
(7)	25°	24 Hours	10	---	---	5	40	---	---	5
(9)	50°	24 Hours	10	4	---	6	35	---	---	4

* "d" Spacings due to Graphite are not included

† O.C. = Opened Circuit

TABLE II

INTENSITIES OF "d" SPACINGS
OBTAINED FROM SINTERED POSITIVE ELECTRODES
DURING CHARGE, OVERCHARGE AND OPENED CIRCUIT STAND*

FIGURE	TREATMENT	"d" SPACINGS					
		6.95	4.40-4.50	3.73-3.62	2.94	2.66	2.44
6	Charge 50 ma	---	16	8	---	---	10
7	Overcharge 50 ma	72	15	8	---	---	---
8	Initial Opened Circuit	18	18	6	5	8	10
9	Opened Circuit-16 hours	---	20	7	---	---	---

* "d" Spacing due to Nickel and Polyethylene are Not Included

TABLE III

INTENSITIES OF "d" SPACINGS
AT VARIOUS STATES OF CHARGE
OF SINTERED POSITIVE ELECTRODES*

FIGURE	TREATMENT	CHG. & DISCHG. RATE	"d" SPACINGS					
			4.50-4.70	3.77-3.73	3.58	2.71	2.47	2.32-2.36
12	200% Chg., 24 hr. stand	1.2 Amps	23	12	---	---	14	---
13	200% Chg., 72 hr. stand	1.2 Amps	30	18	---	---	15	---
14	10% Beyond Vigorous Gas.	1.2 Amps	25	7	---	8	17	11
15	20% Below Vigorous Gas.	1.2 Amps	28	8	---	---	19	7
16	200% Chg., 50% Dischg.	1.2 Amps	24	8	---	---	14	12
17	200% Chg., 75% Dischg.	1.2 Amps	25	7	---	---	10	8
18	200% Chg., Complete Dischg.	1.2 Amps	20	---	5	---	7	6
19	200% Charge	0.150 Amps	18	---	---	---	10	---
20	10% Beyond Vigorous Gas.	0.150 Amps	18	---	---	---	15	---
21	11 Hour Charge	0.150 Amps	8	8	---	---	13	8

* "d" Spacings due to Nickel and Polyethylene are not included

TABLE III - Continued

"d" SPACINGS

<u>FIGURE</u>	<u>TREATMENT</u>	<u>CHG. & DISCHG. RATE</u>	<u>4.50-4.70</u>	<u>3.77-3.73</u>	<u>3.58</u>	<u>2.71</u>	<u>2.47</u>	<u>2.32-2.36</u>
22	20% Below Vigorous Ga.	0.150 Amps	5	8	---	---	10	6
23	8 Hour Charge	0.150 Amps	8	---	---	---	16	10
24	200% Chg., 50% Dischg.	0.150 Amps	5	---	---	---	15	8
25	200% Chg., 75% Dischg.	0.150 Amps	8	---	---	---	15	7
26	200% Chg., Complete Dischg.	0.150 Amps	4	---	---	10	---	8

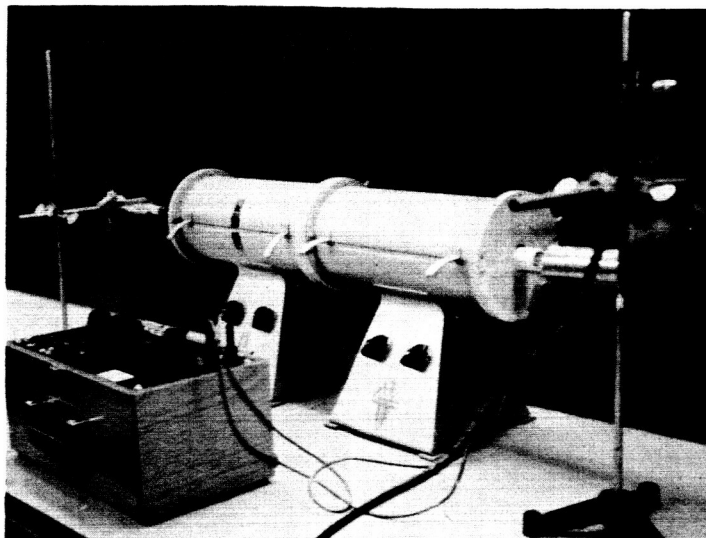


FIGURE 1 APPARATUS SET UP FOR HYDROGEN DETERMINATION

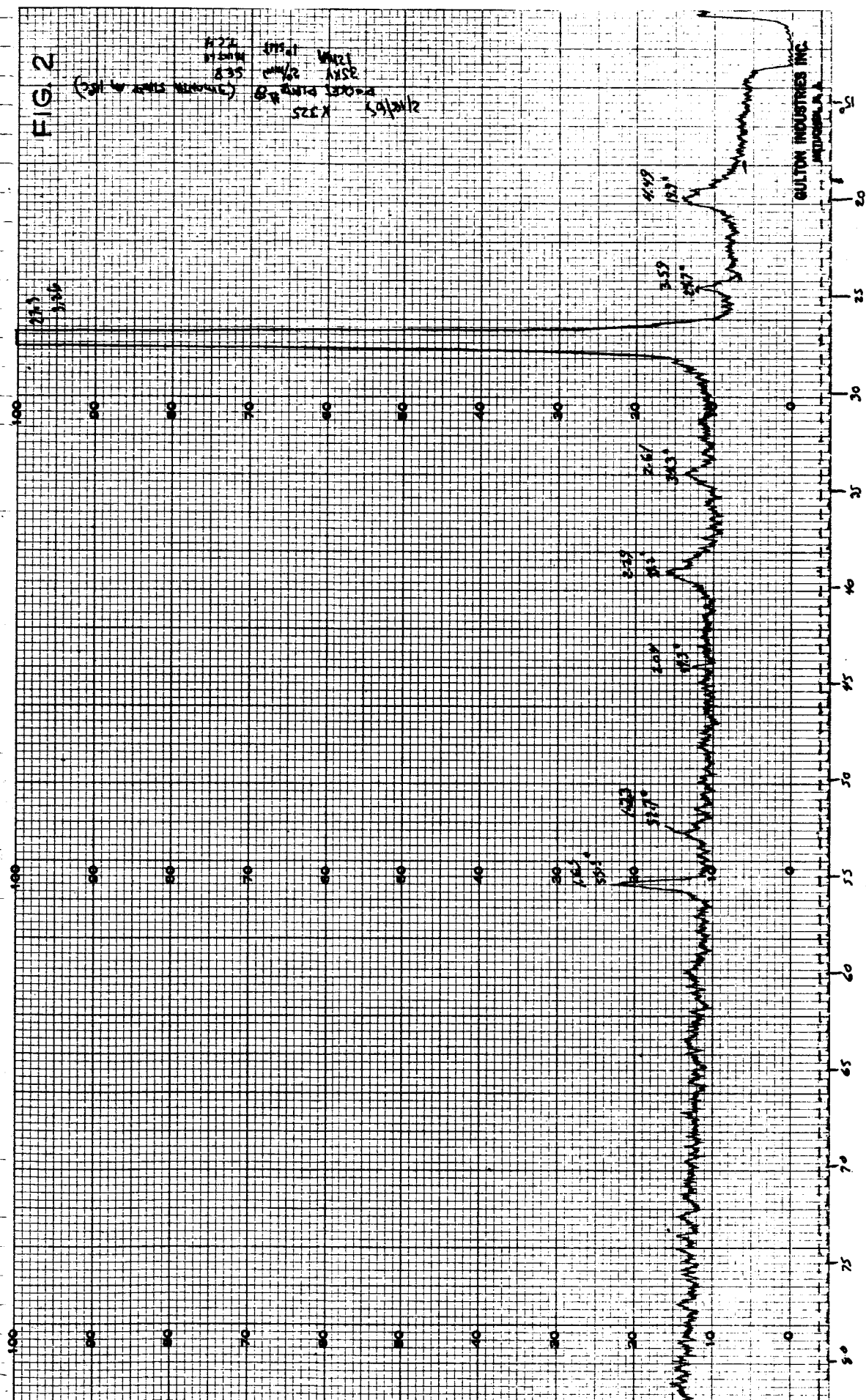
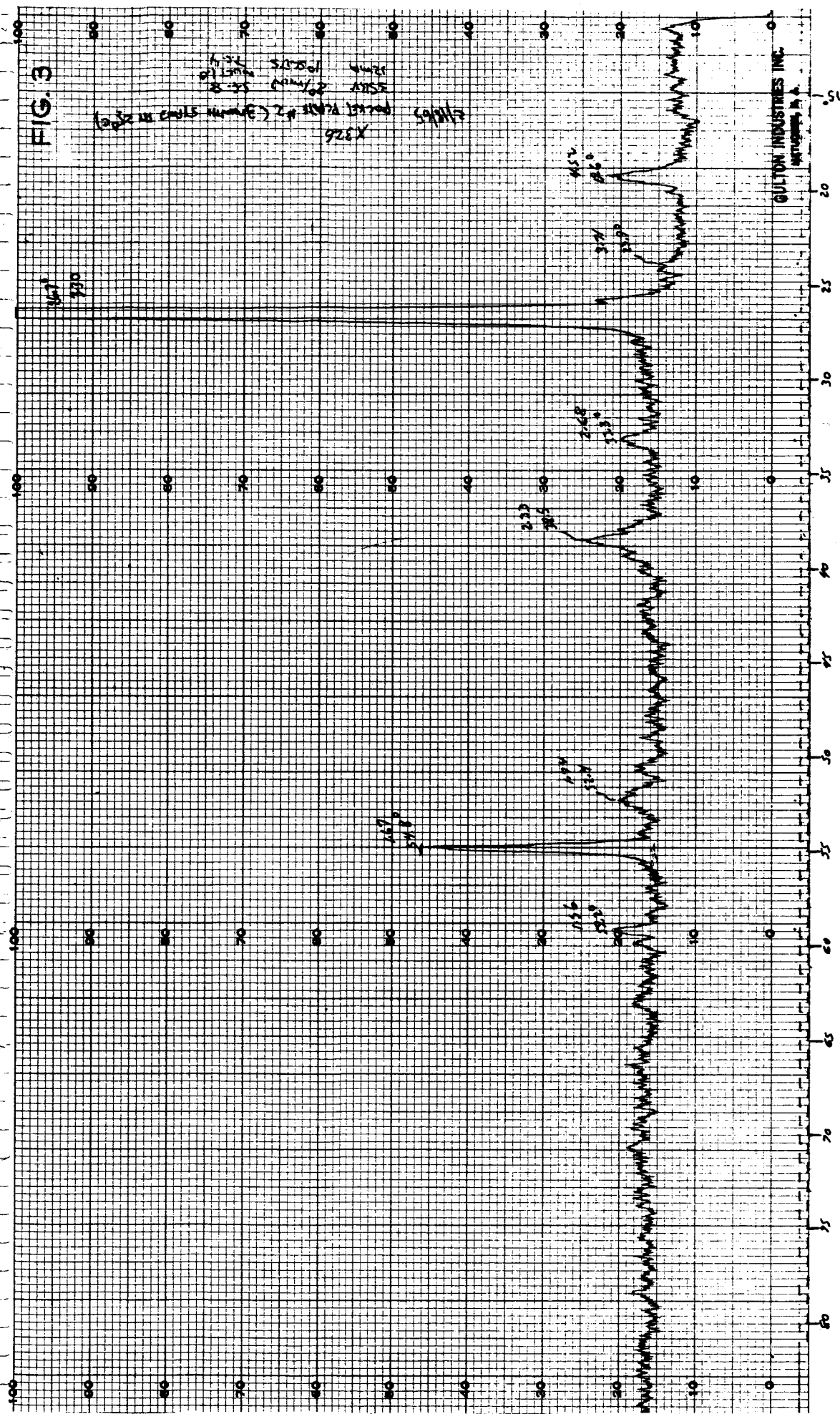


FIG. 3



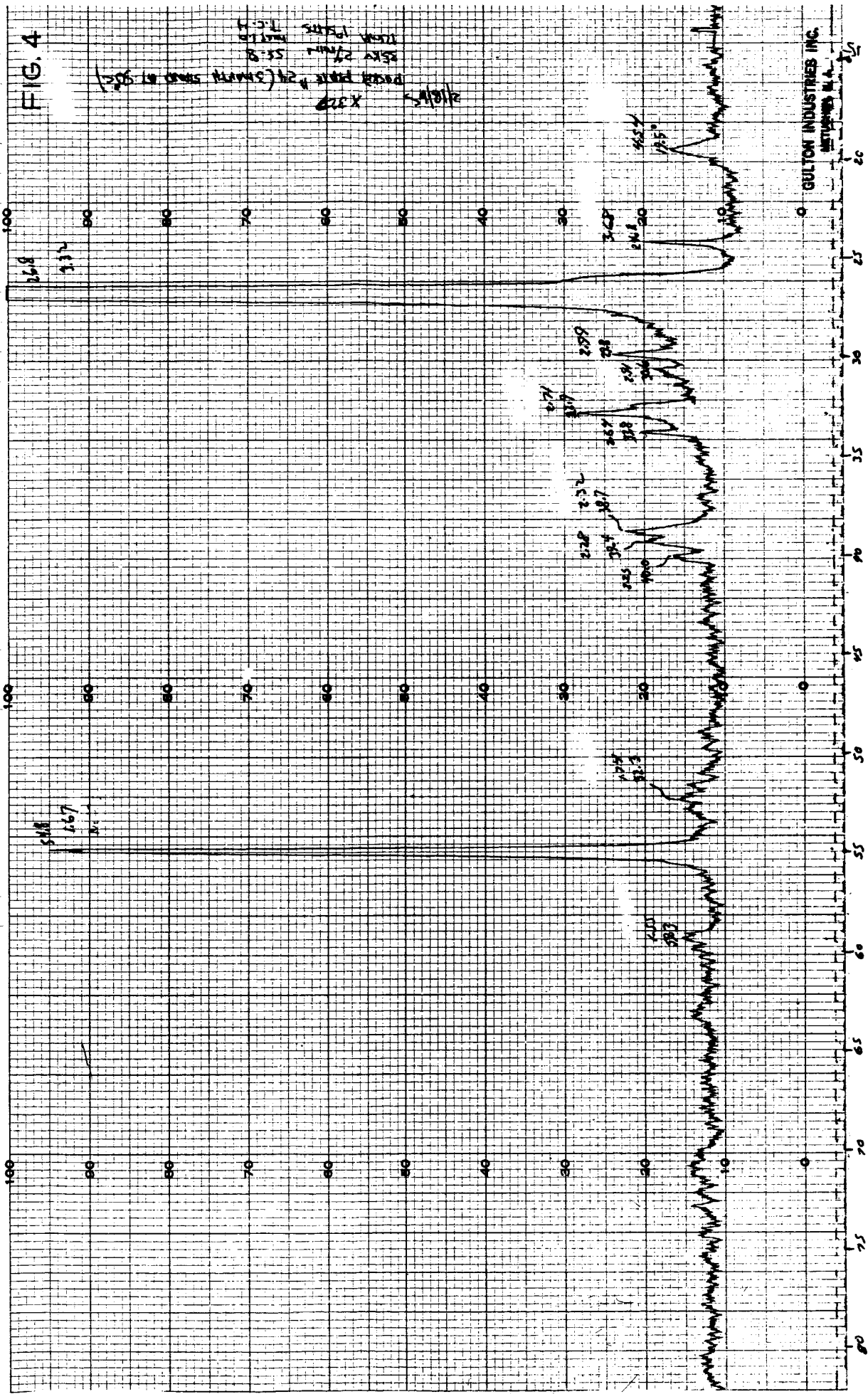
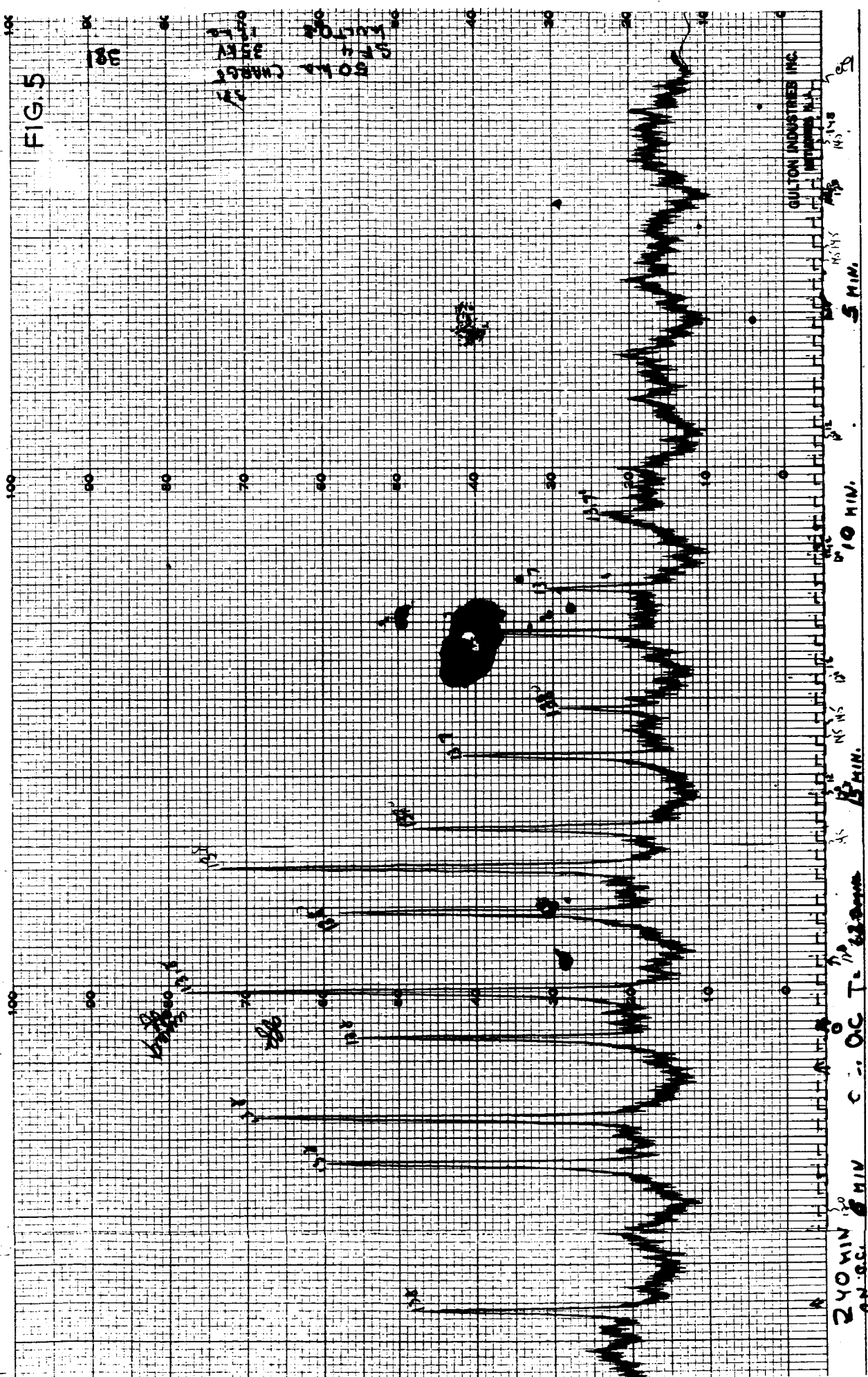


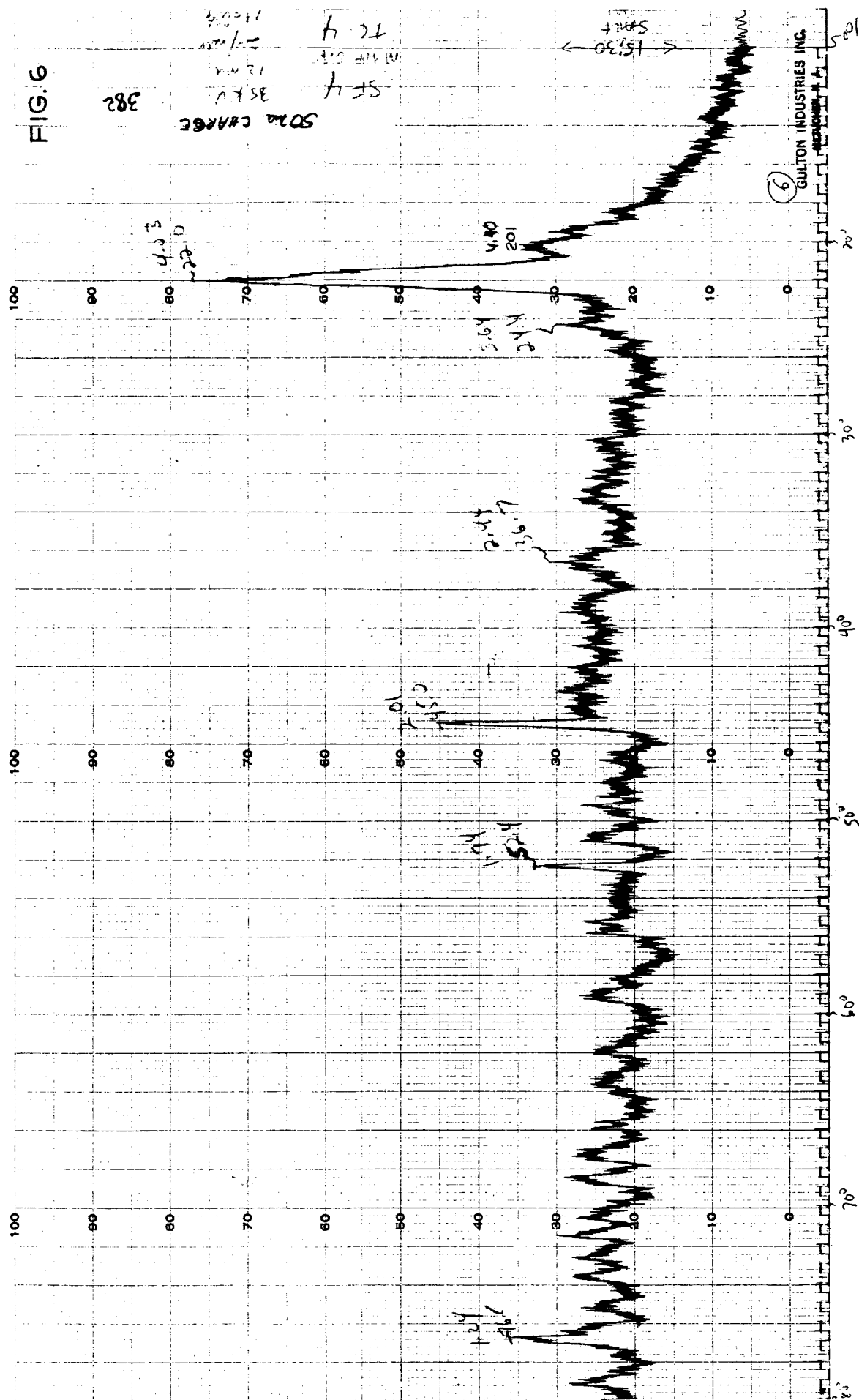
FIG. 4

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FIG. 5





9. 6. 11

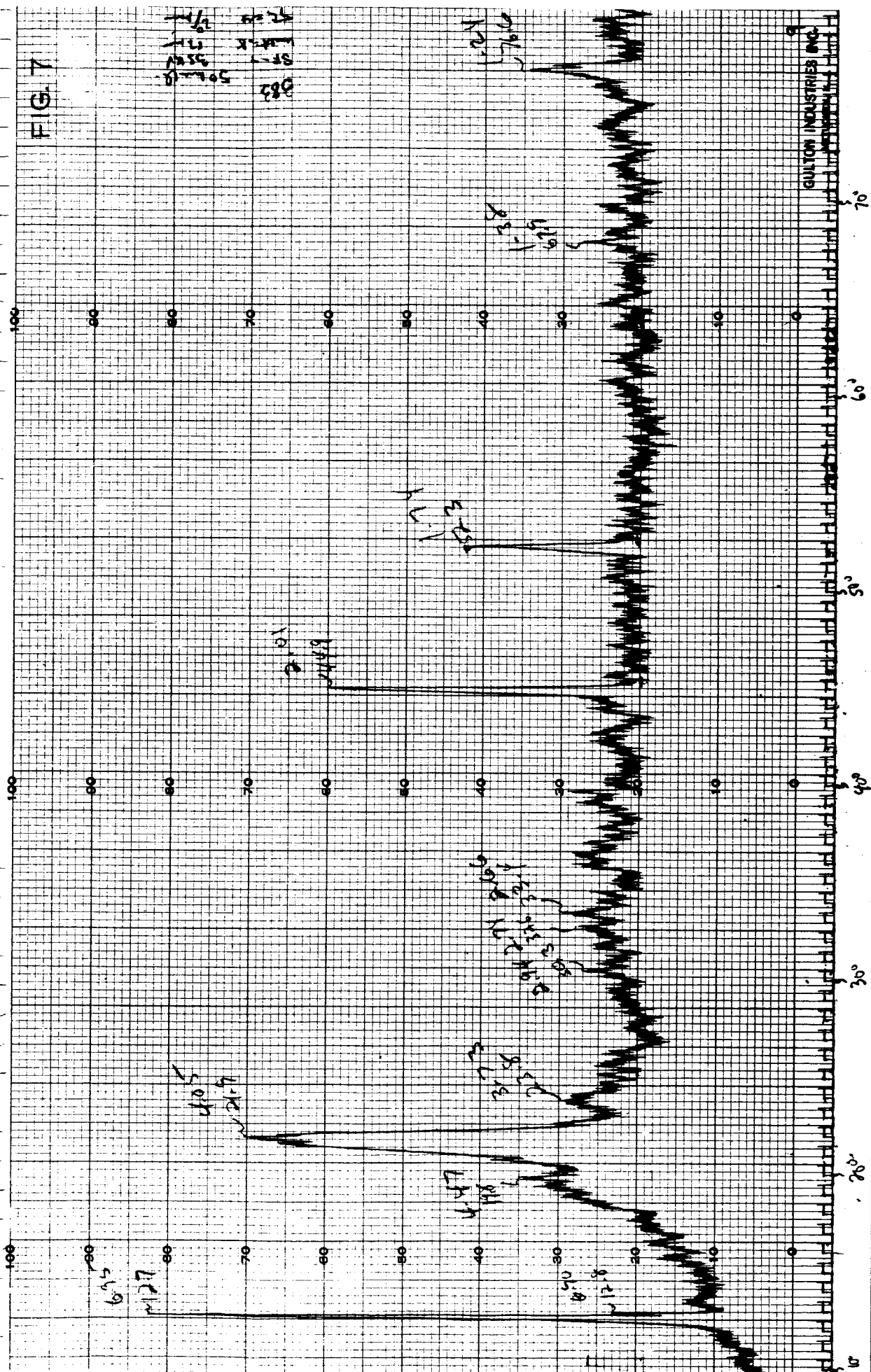
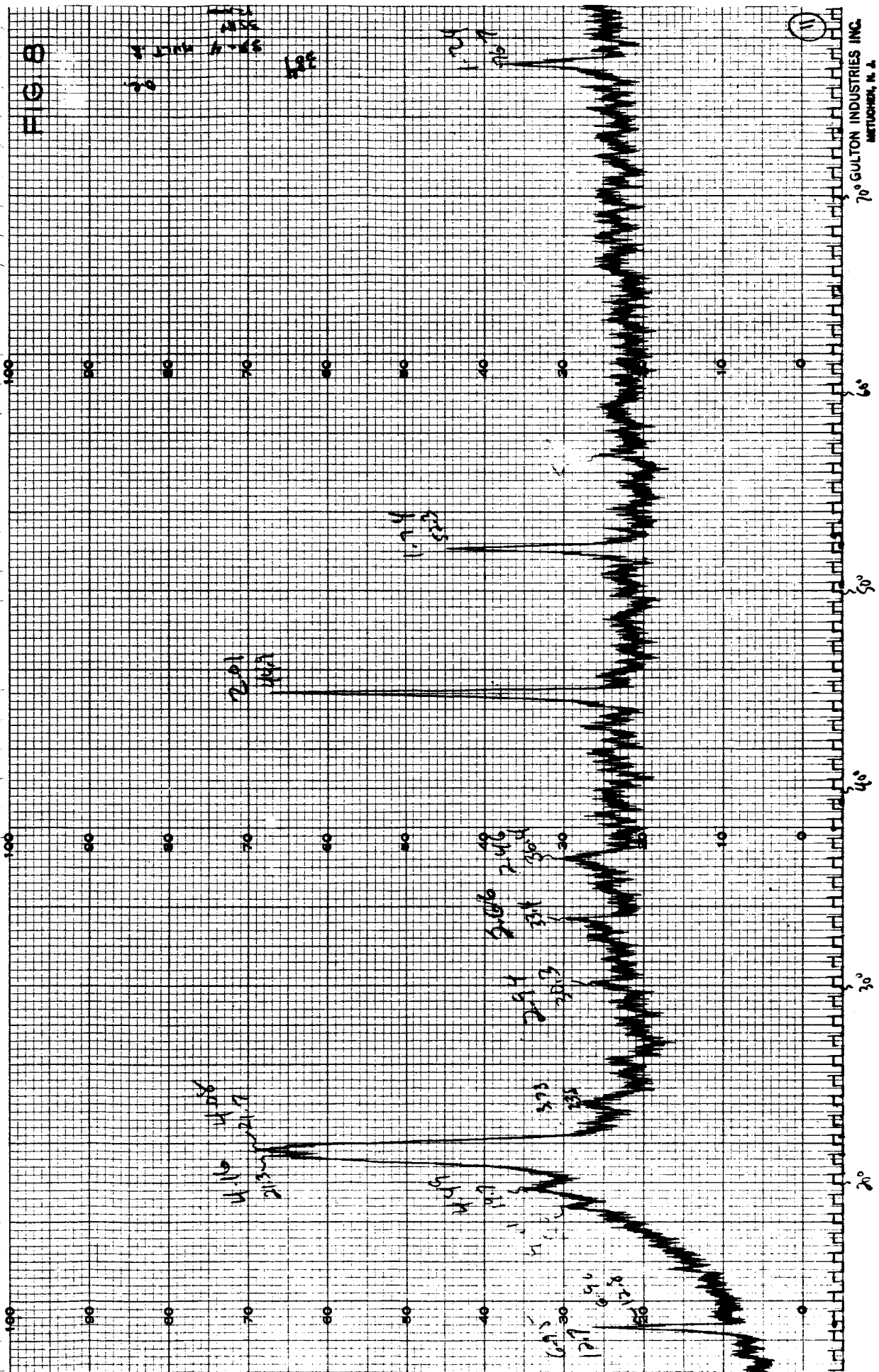
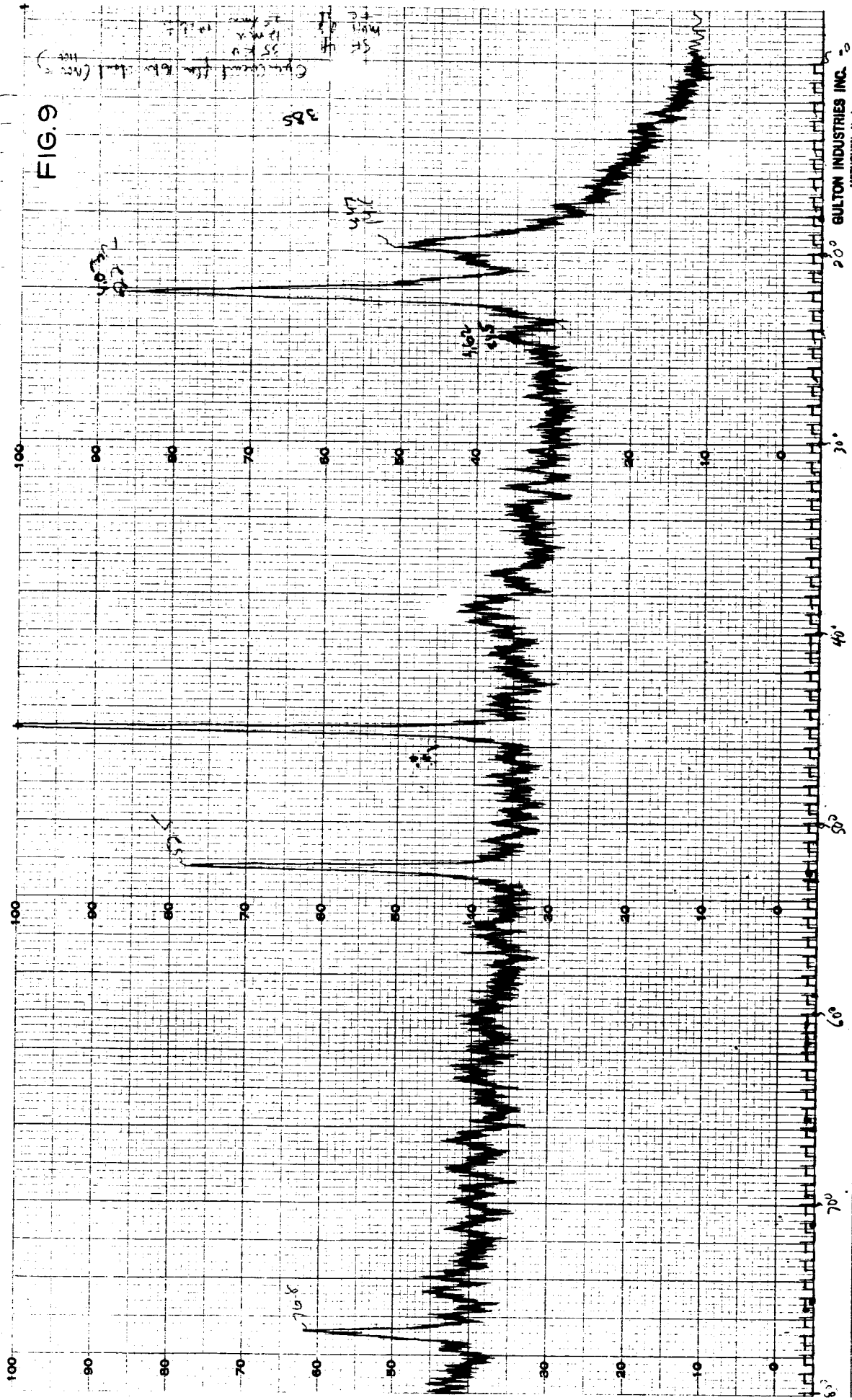
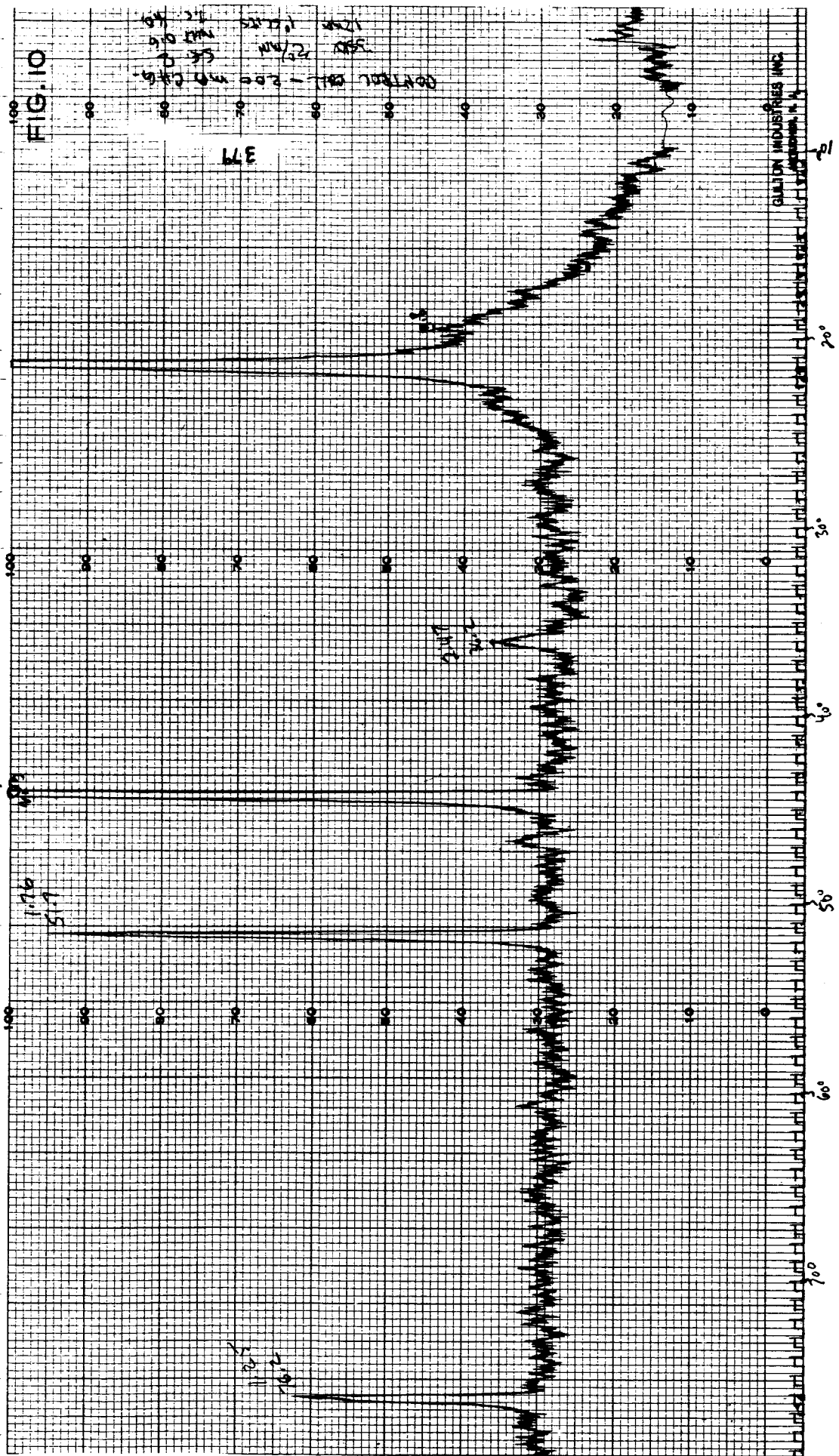
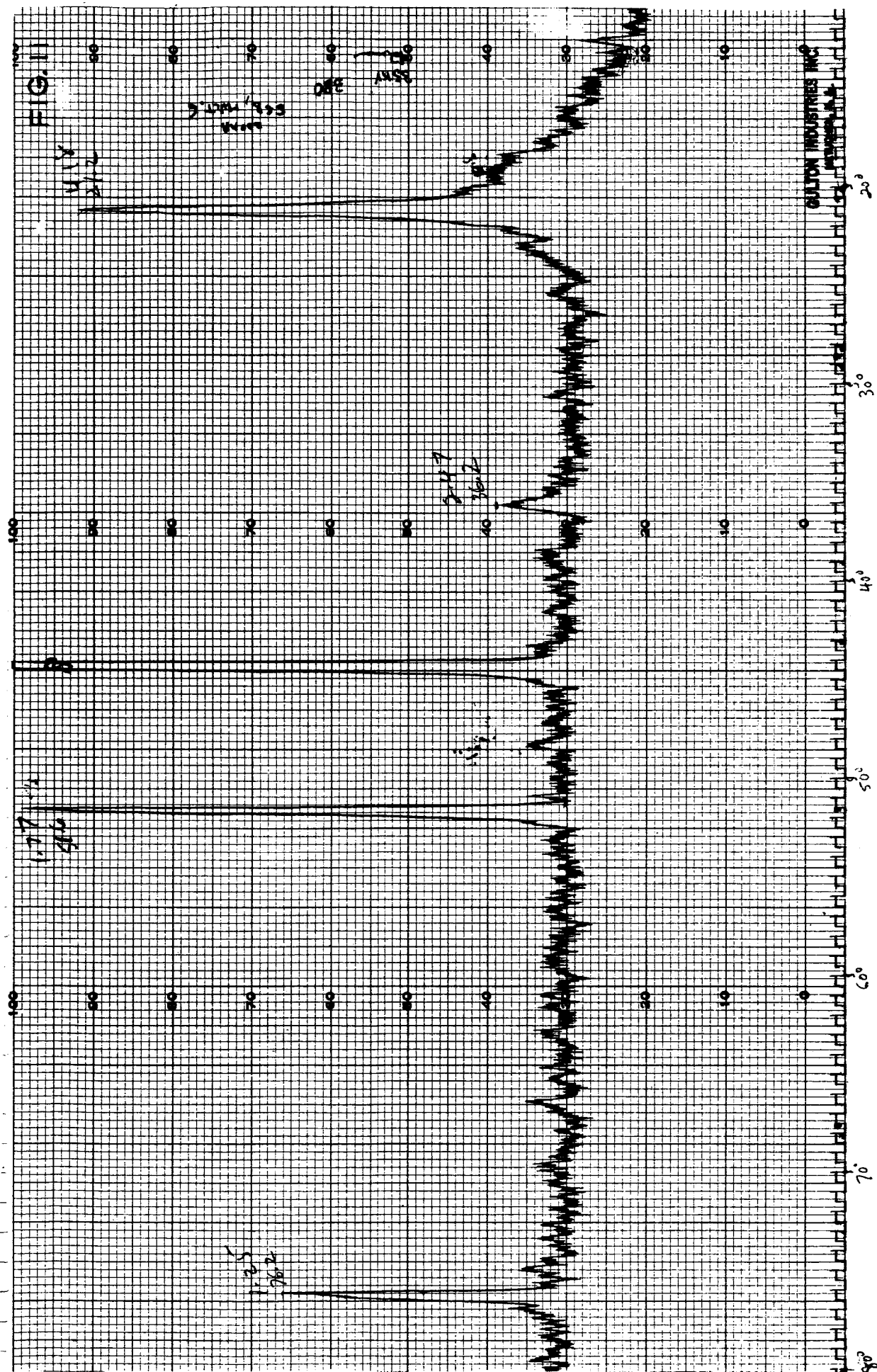


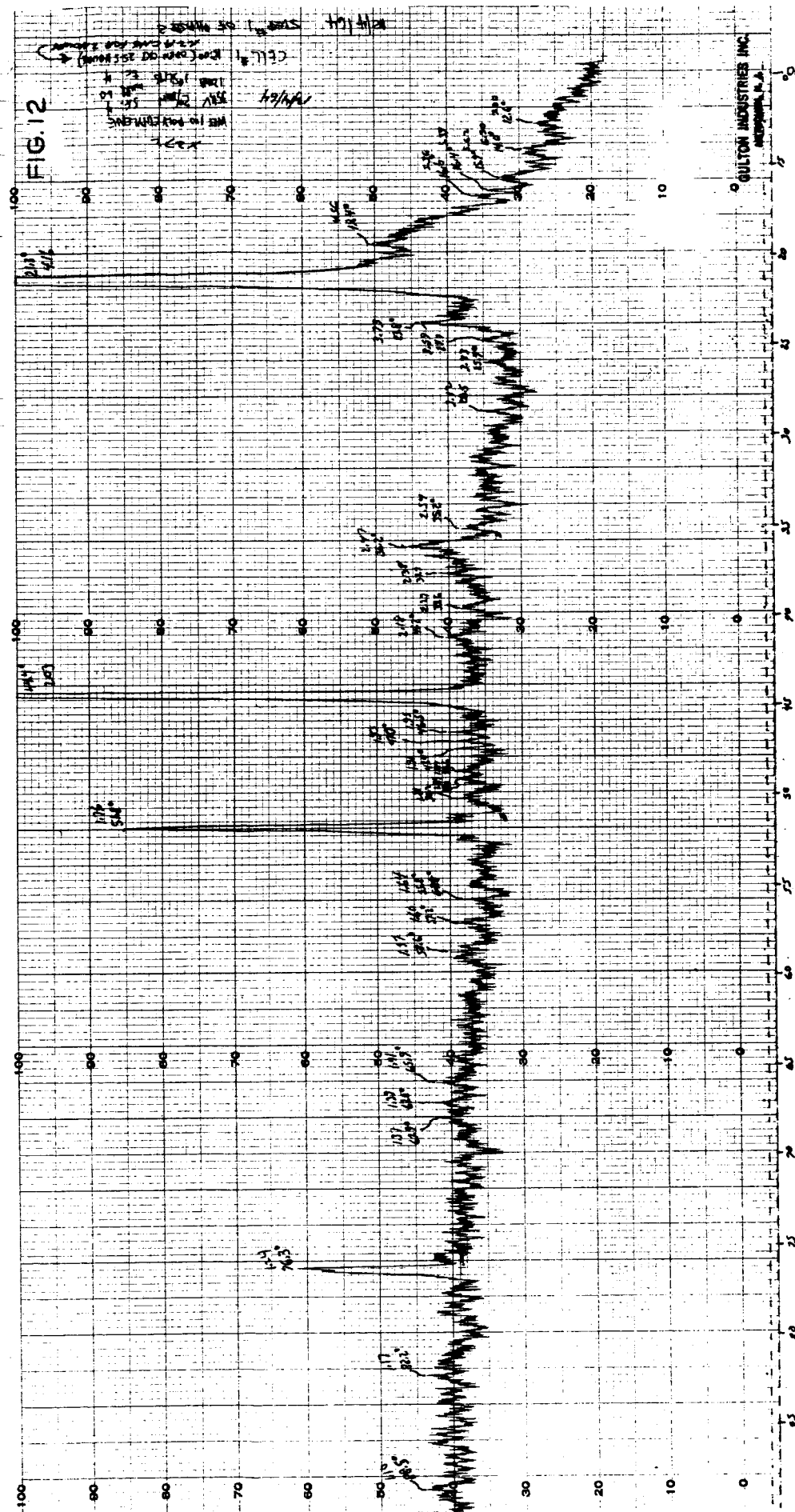
FIG 8

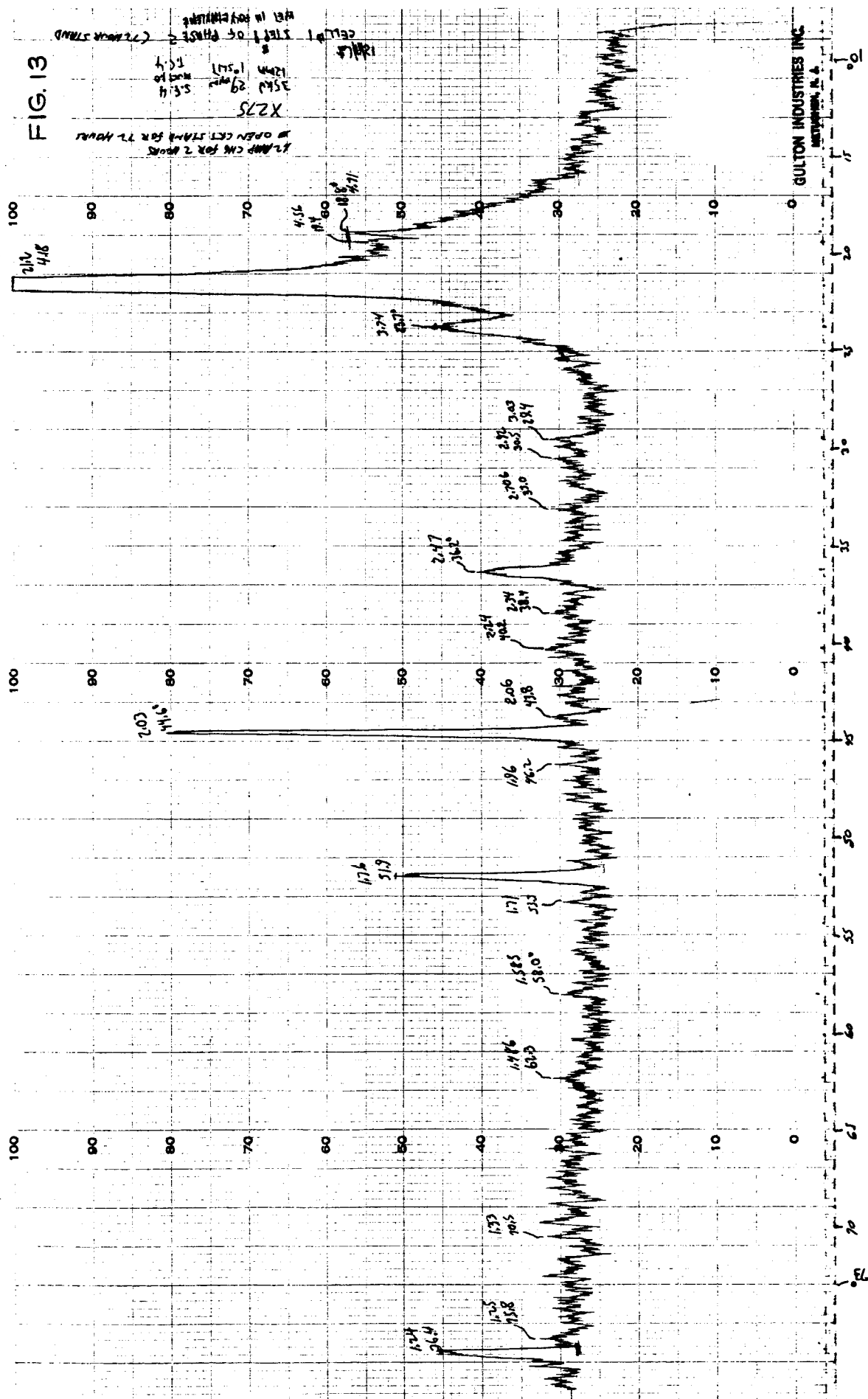


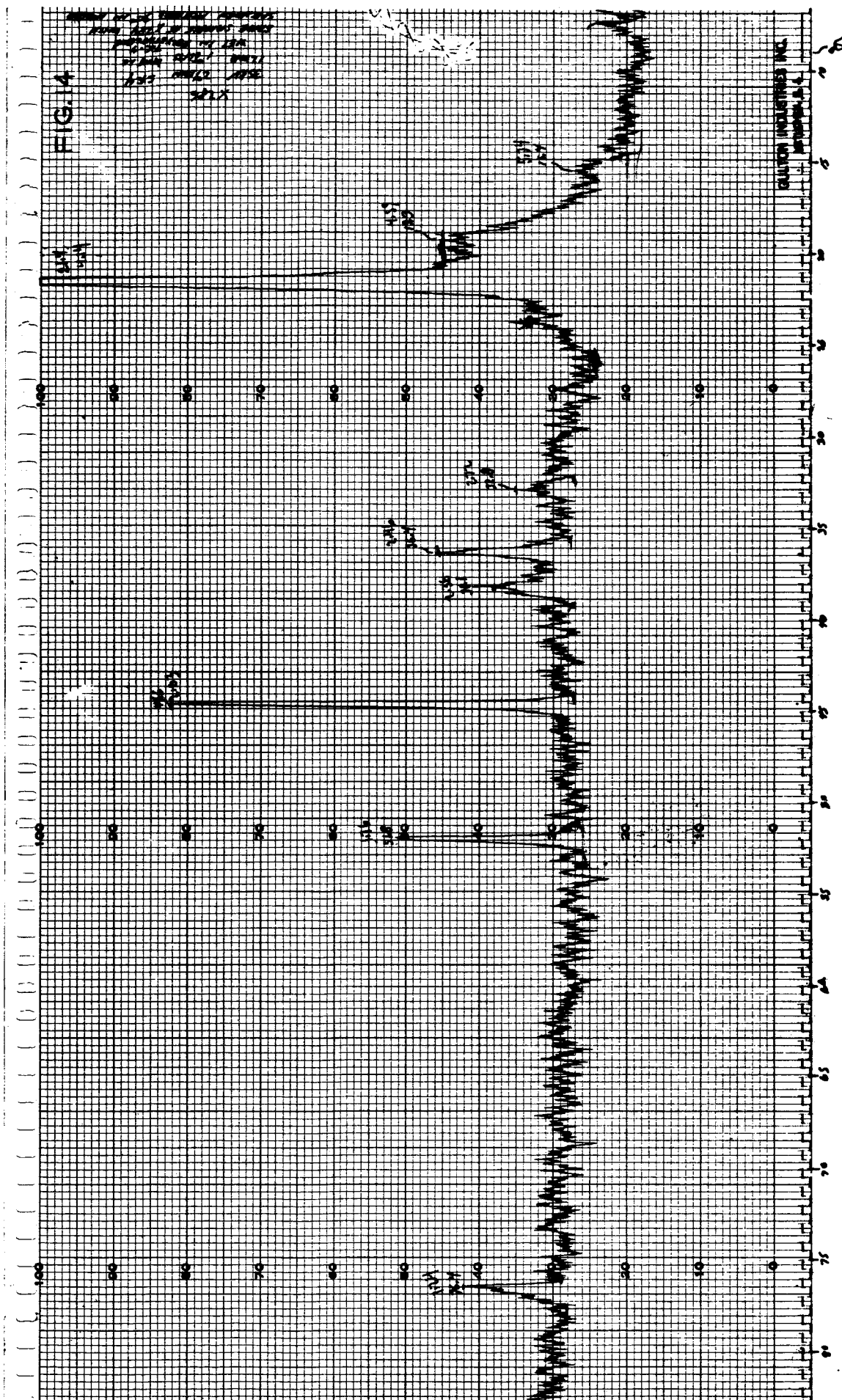


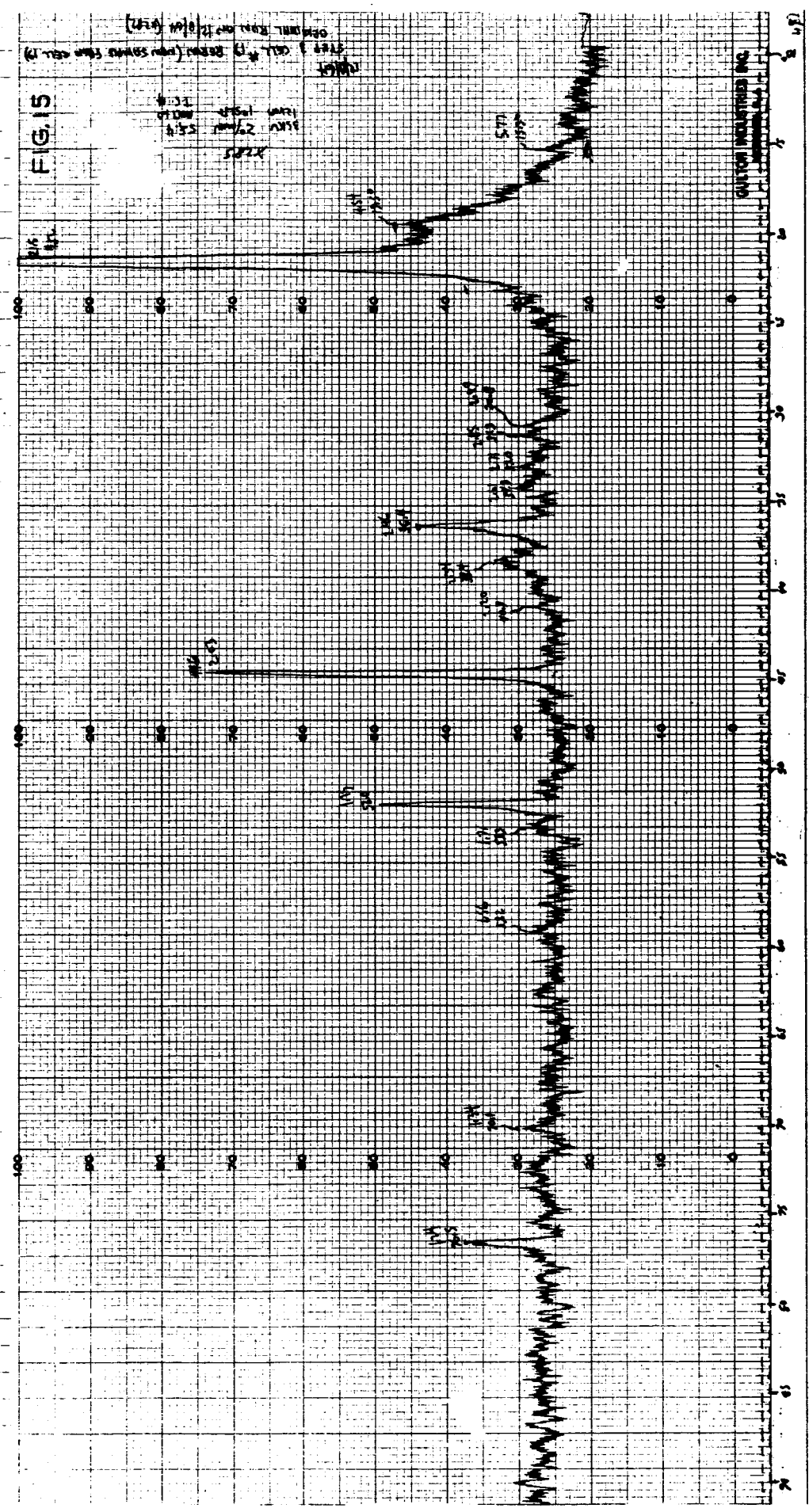


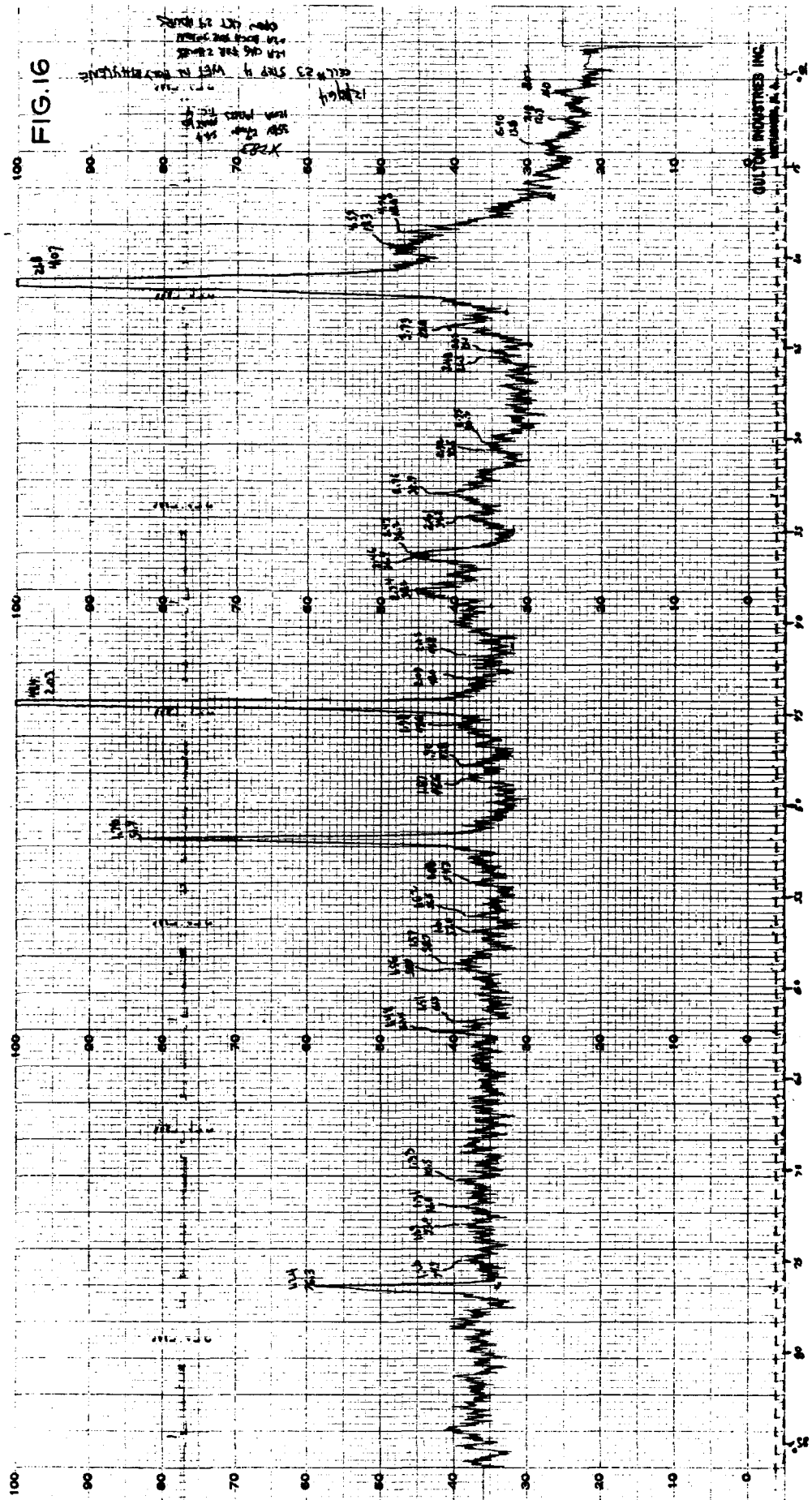


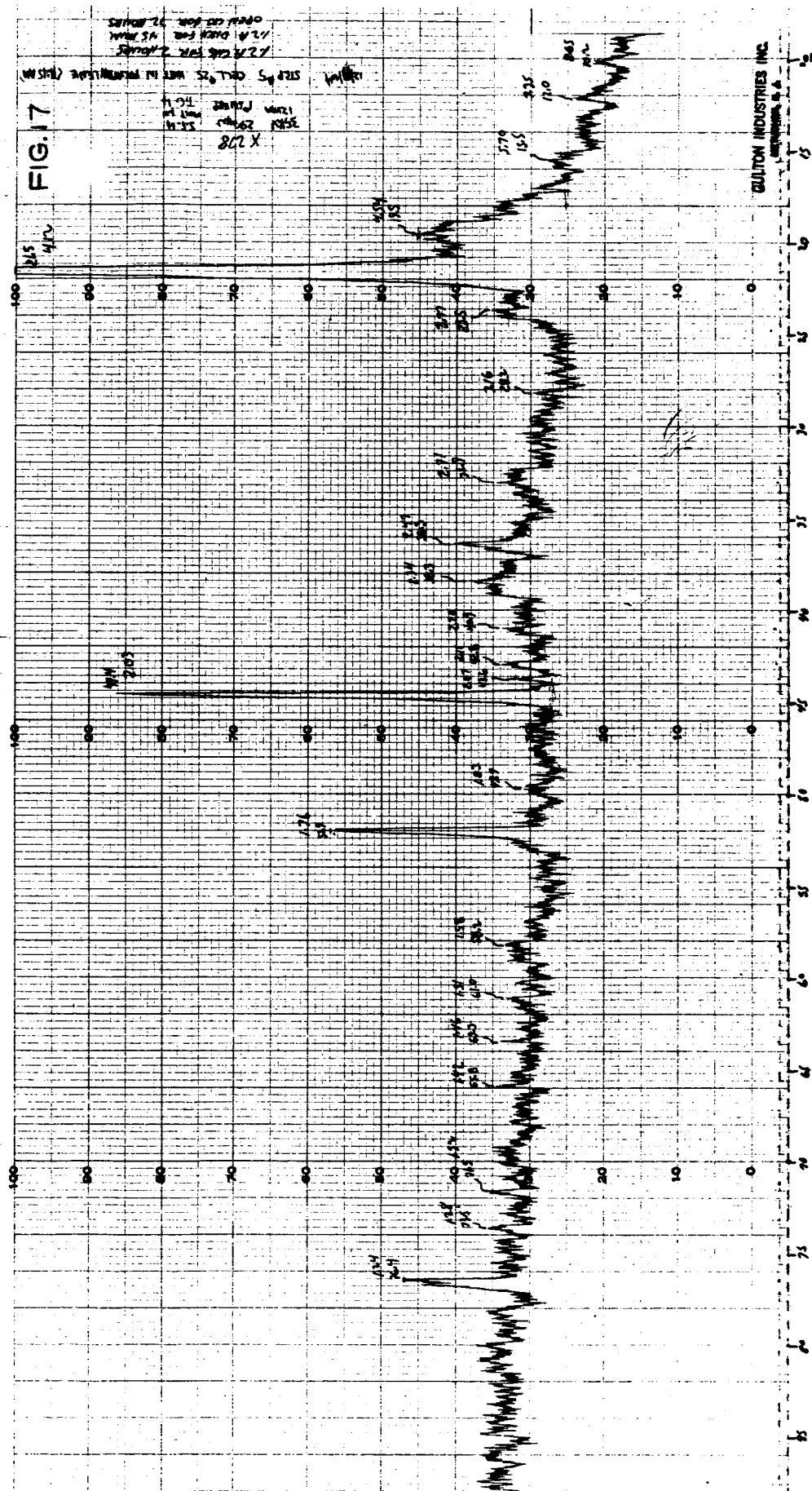


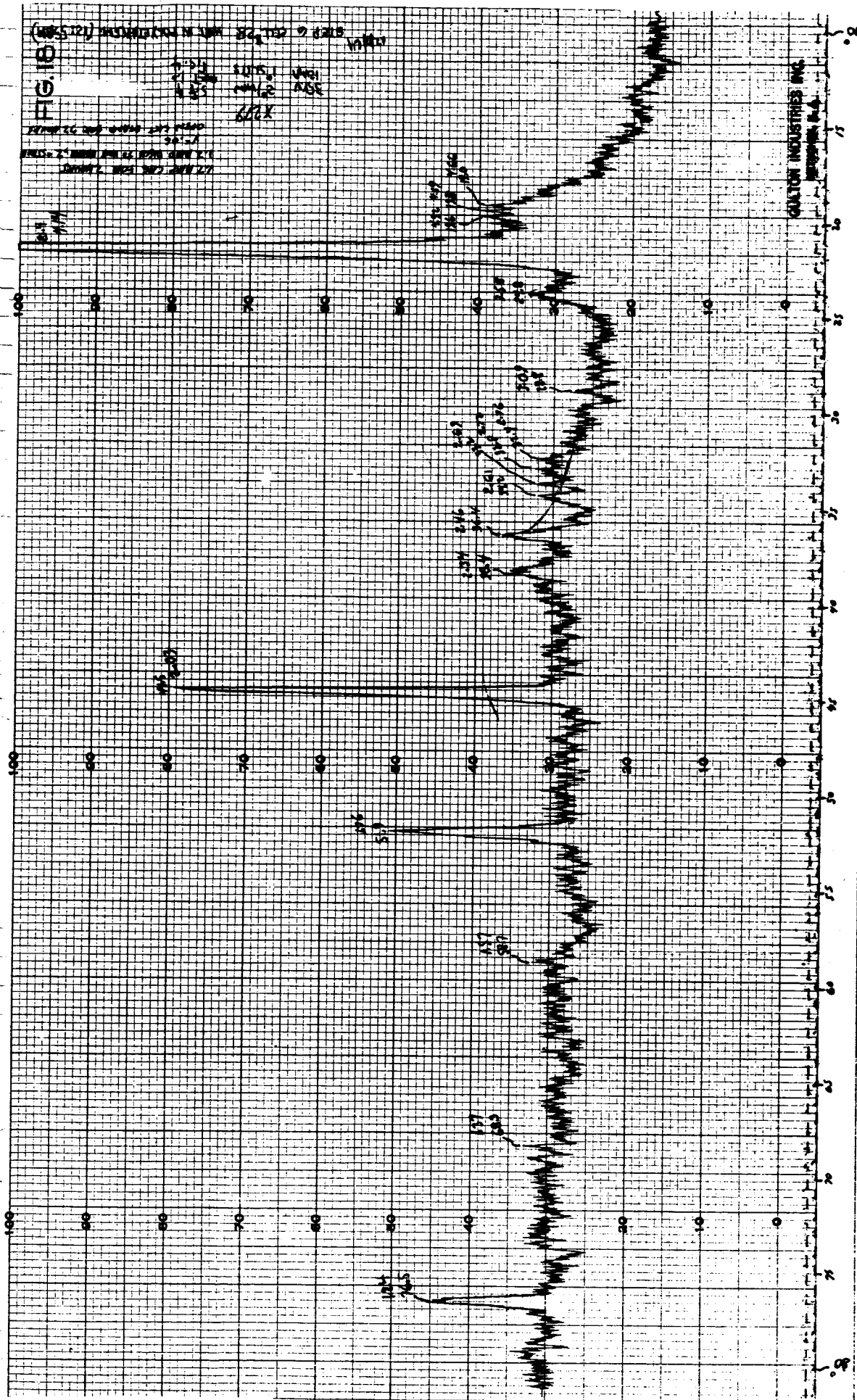


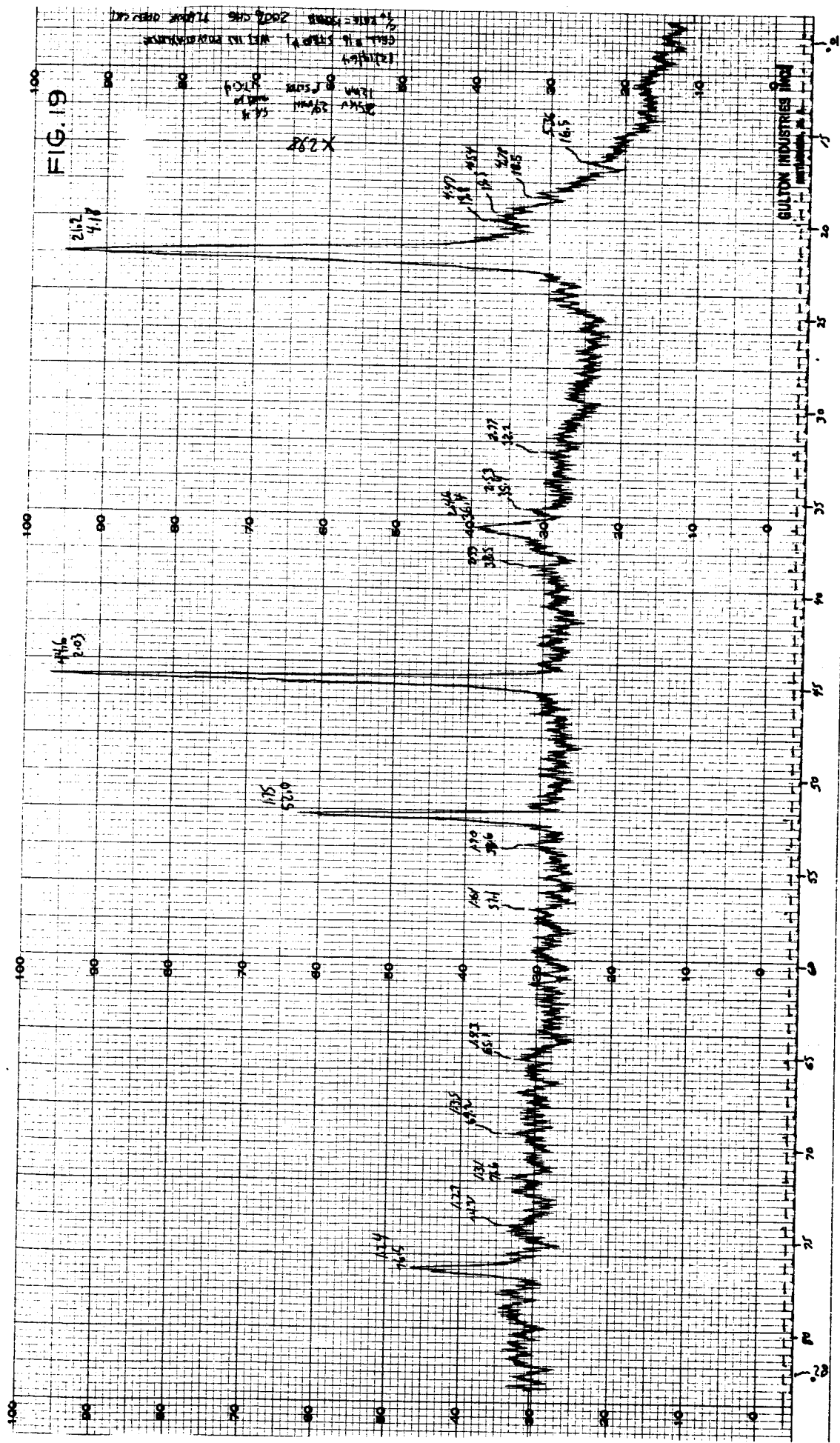












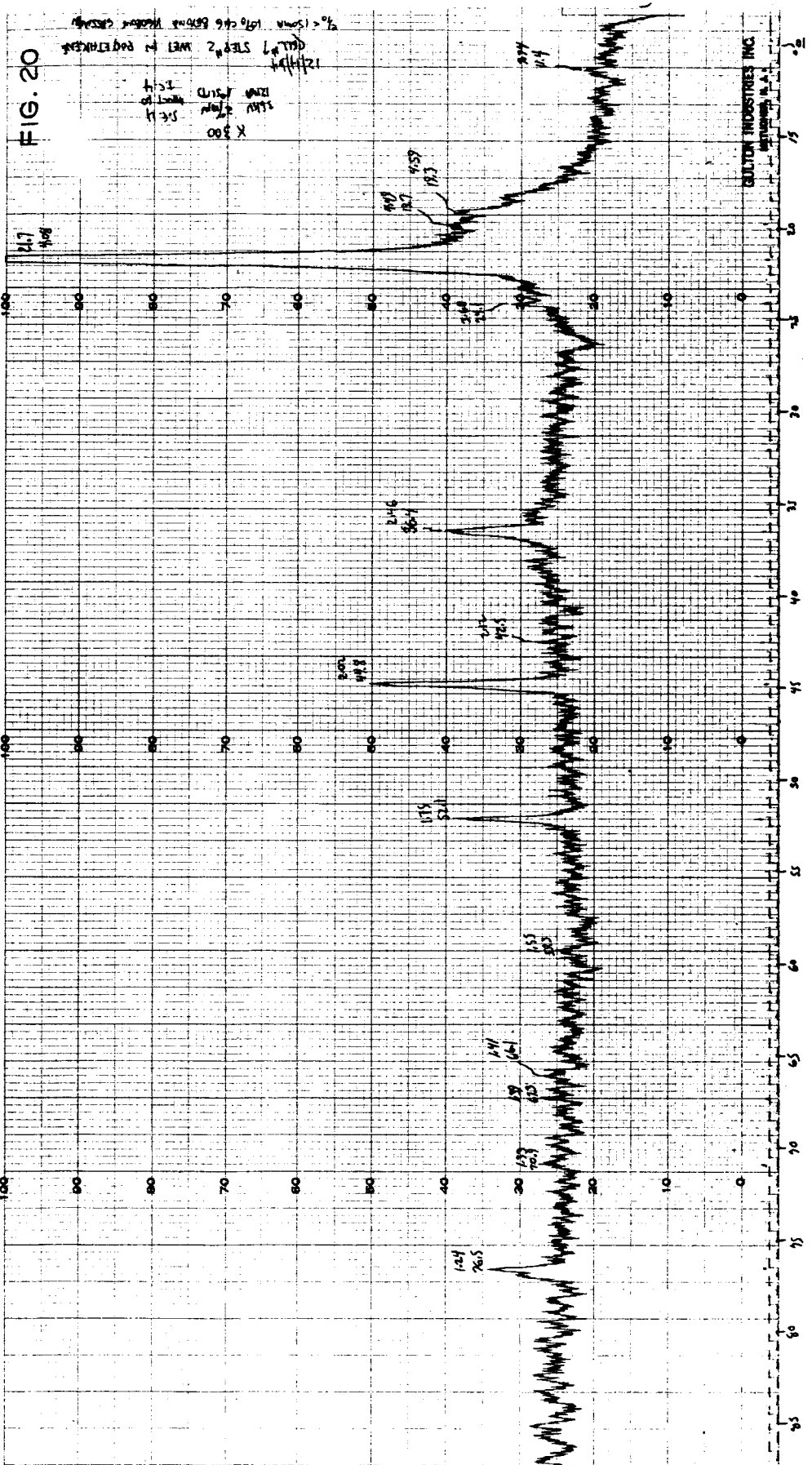
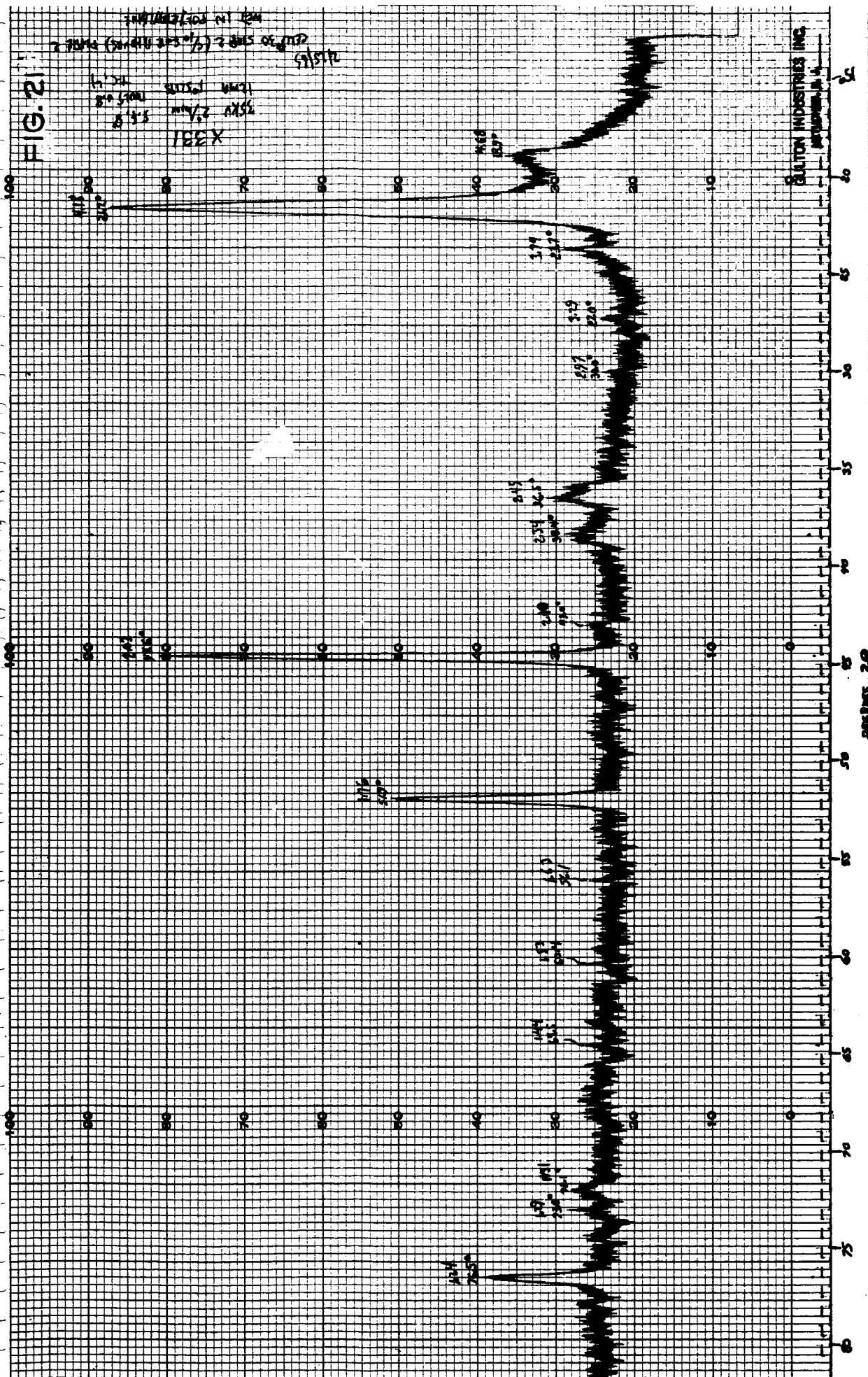
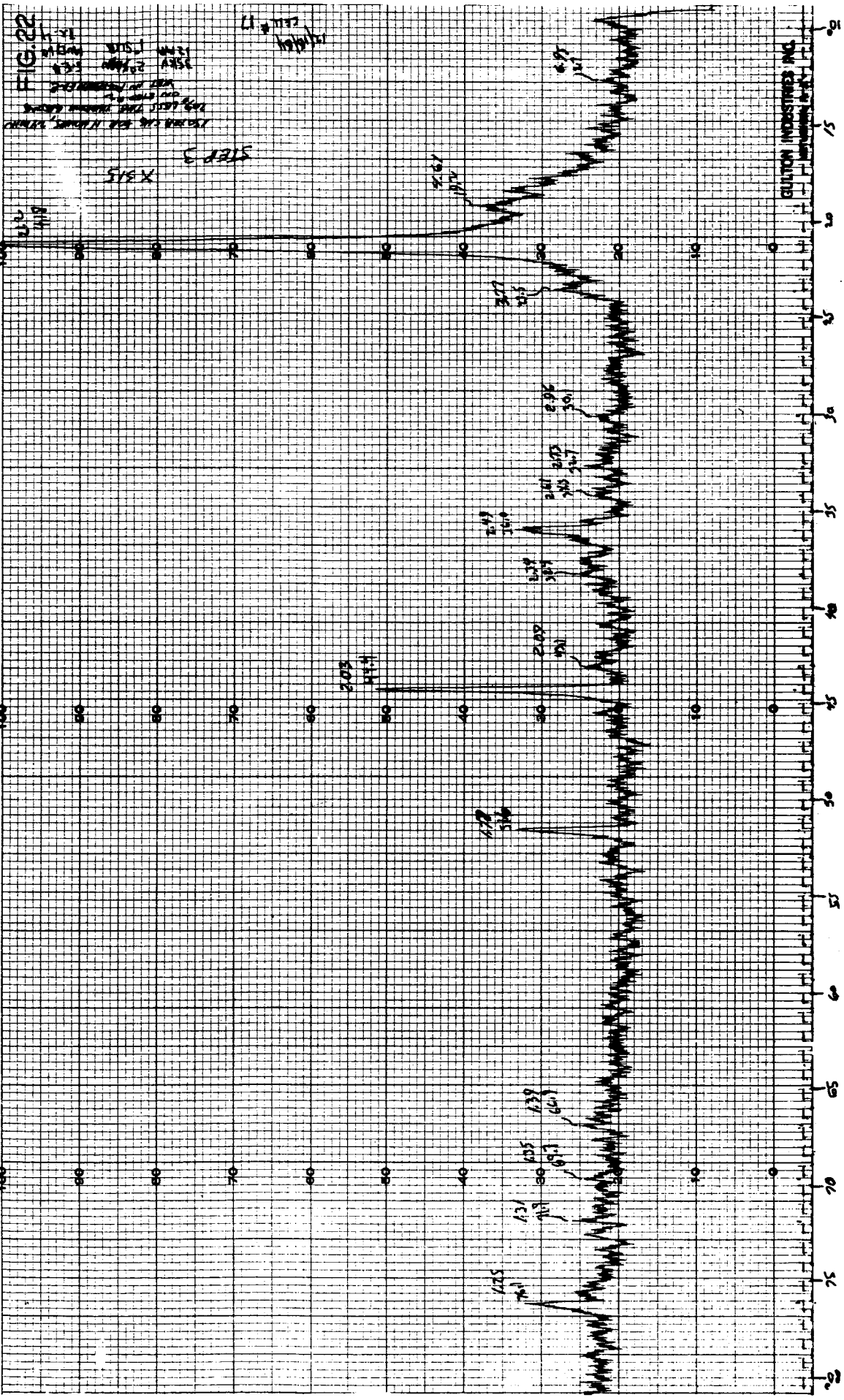


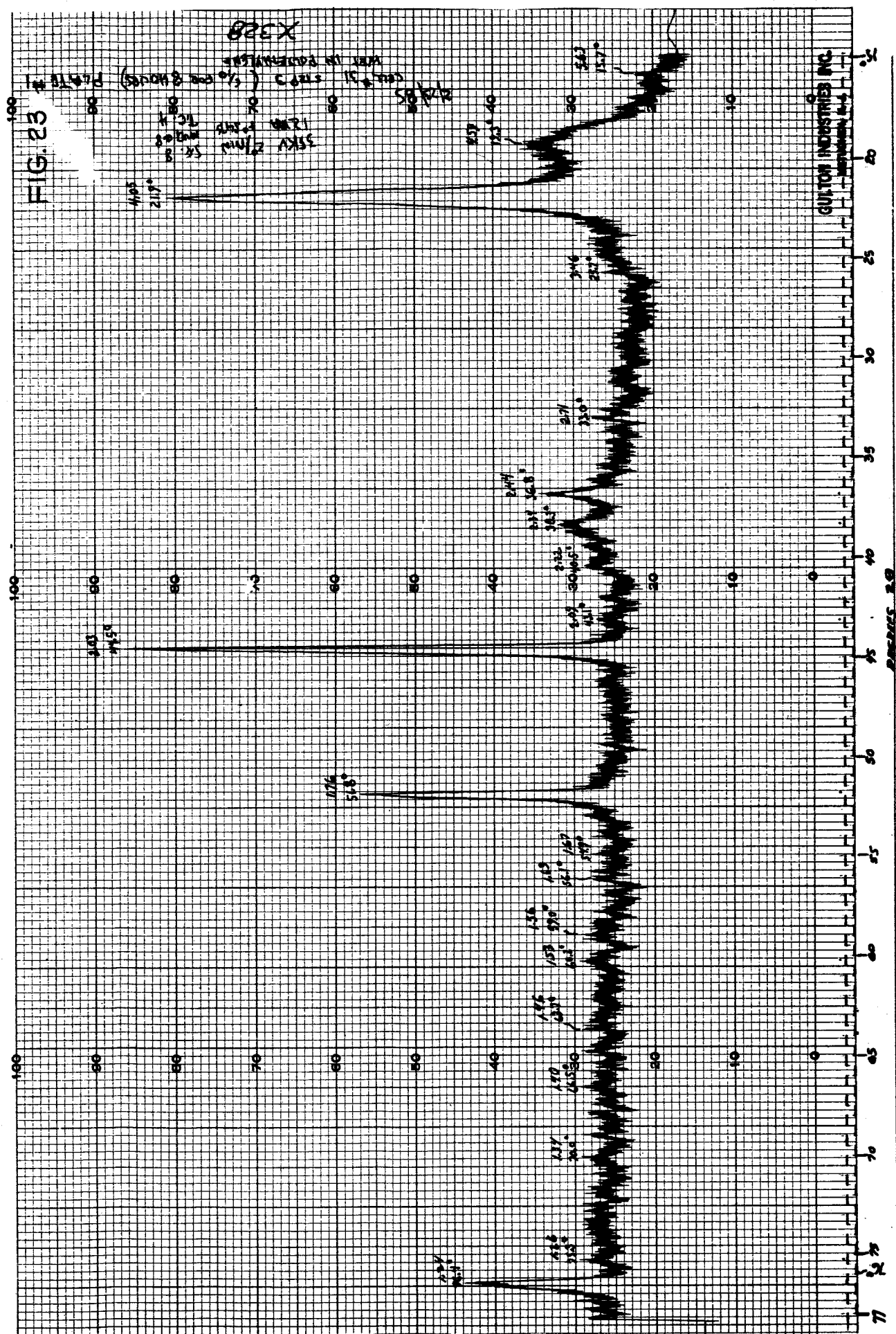
FIG. 21

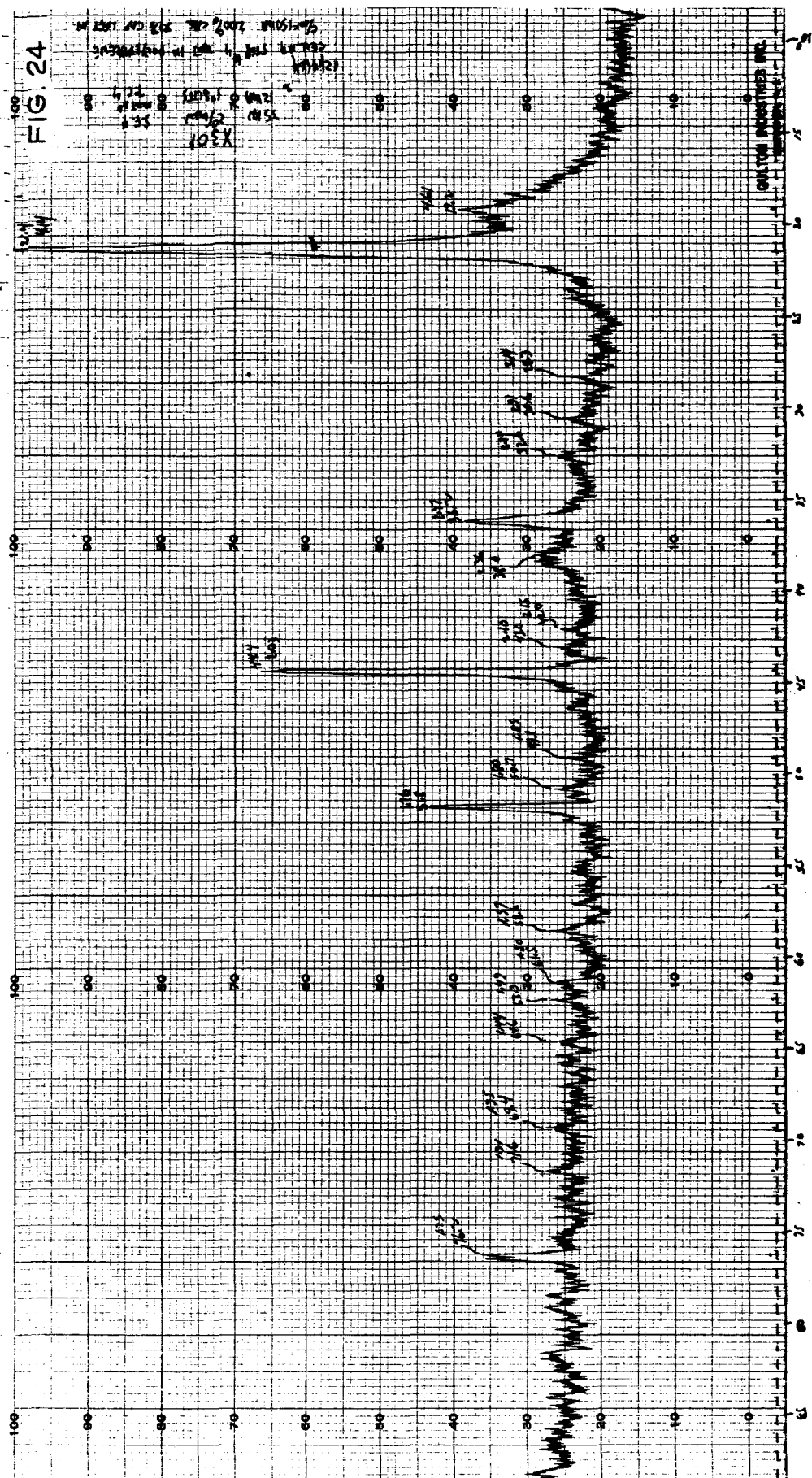


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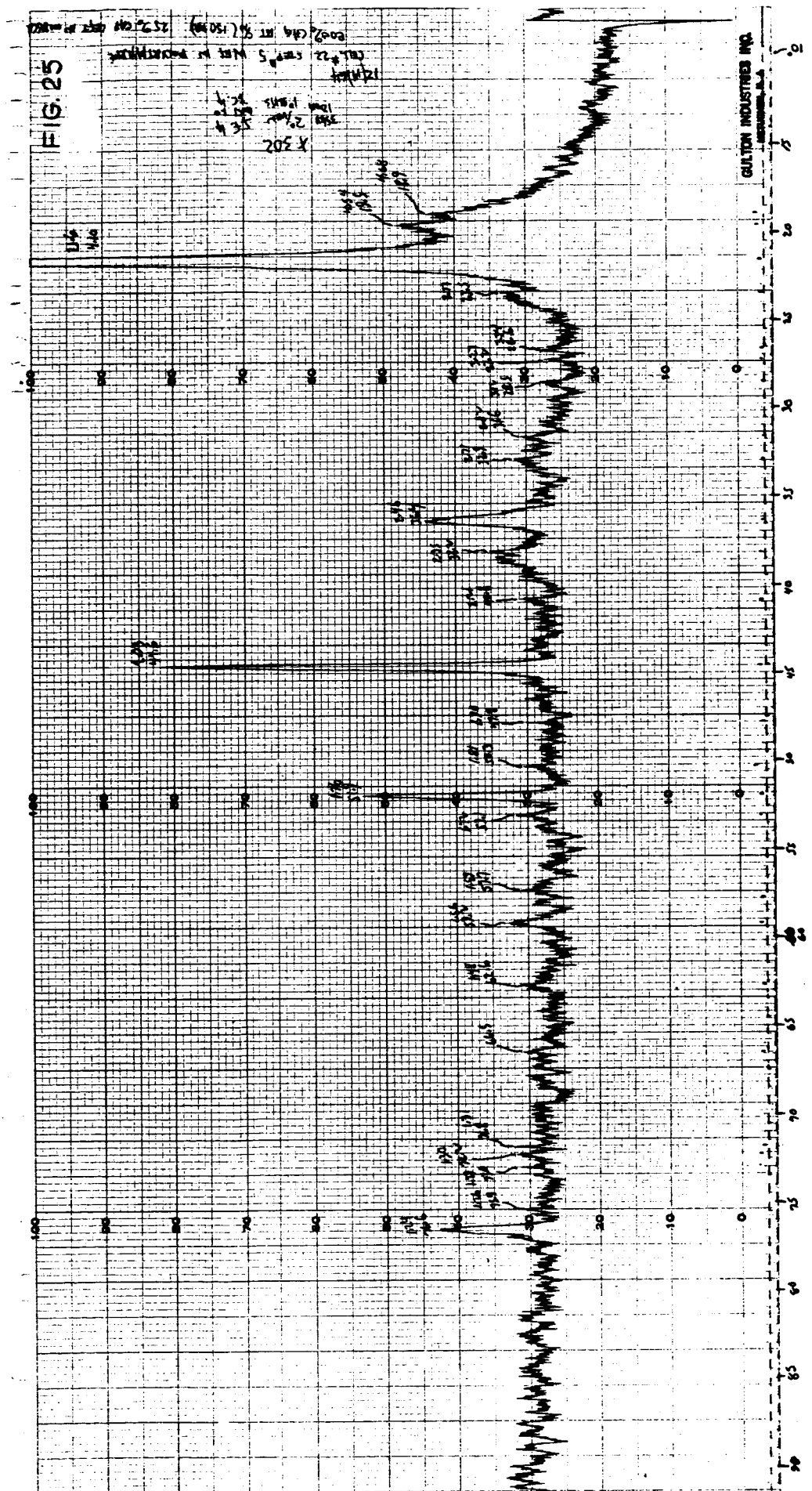


FIG. 27

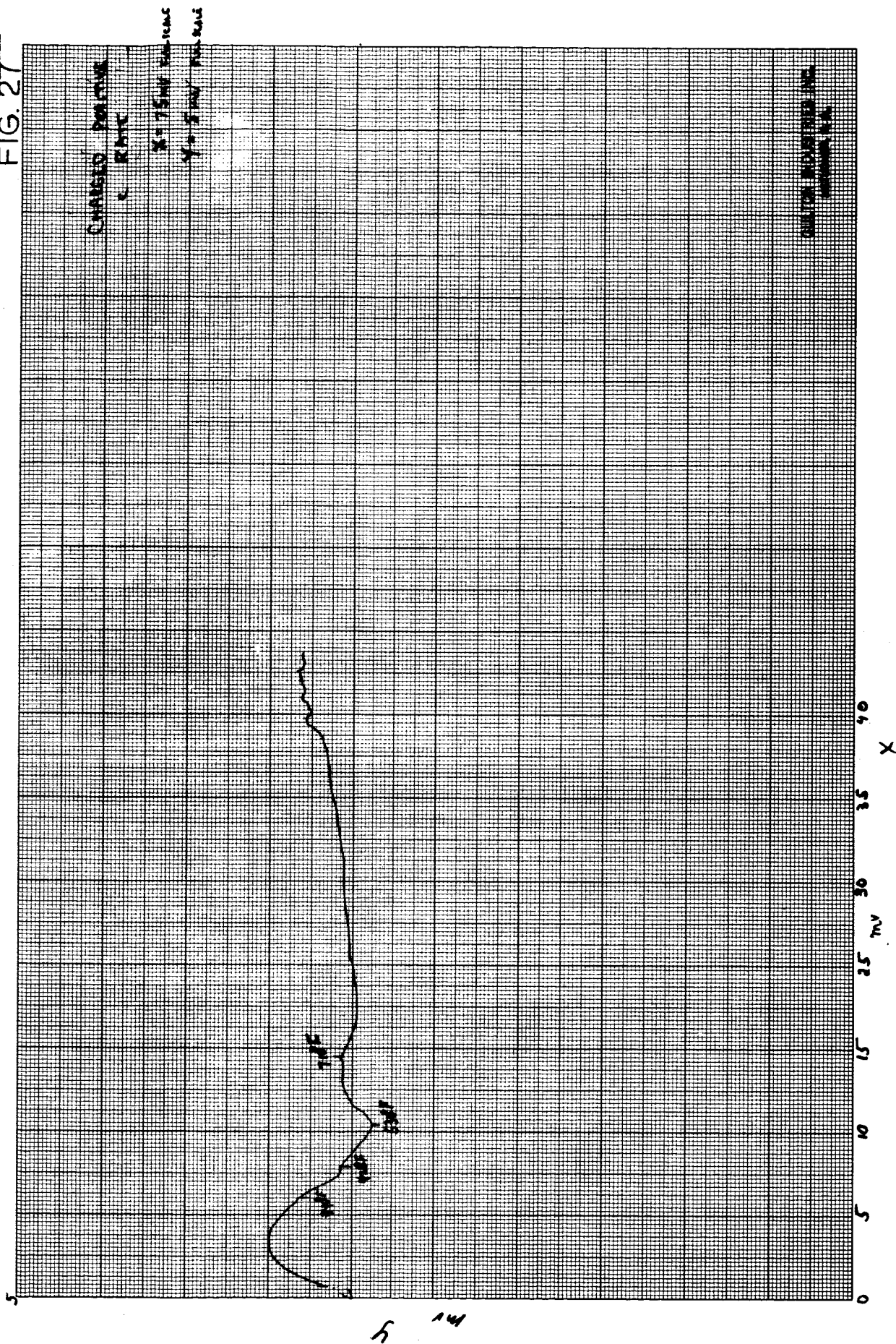


FIG. 28

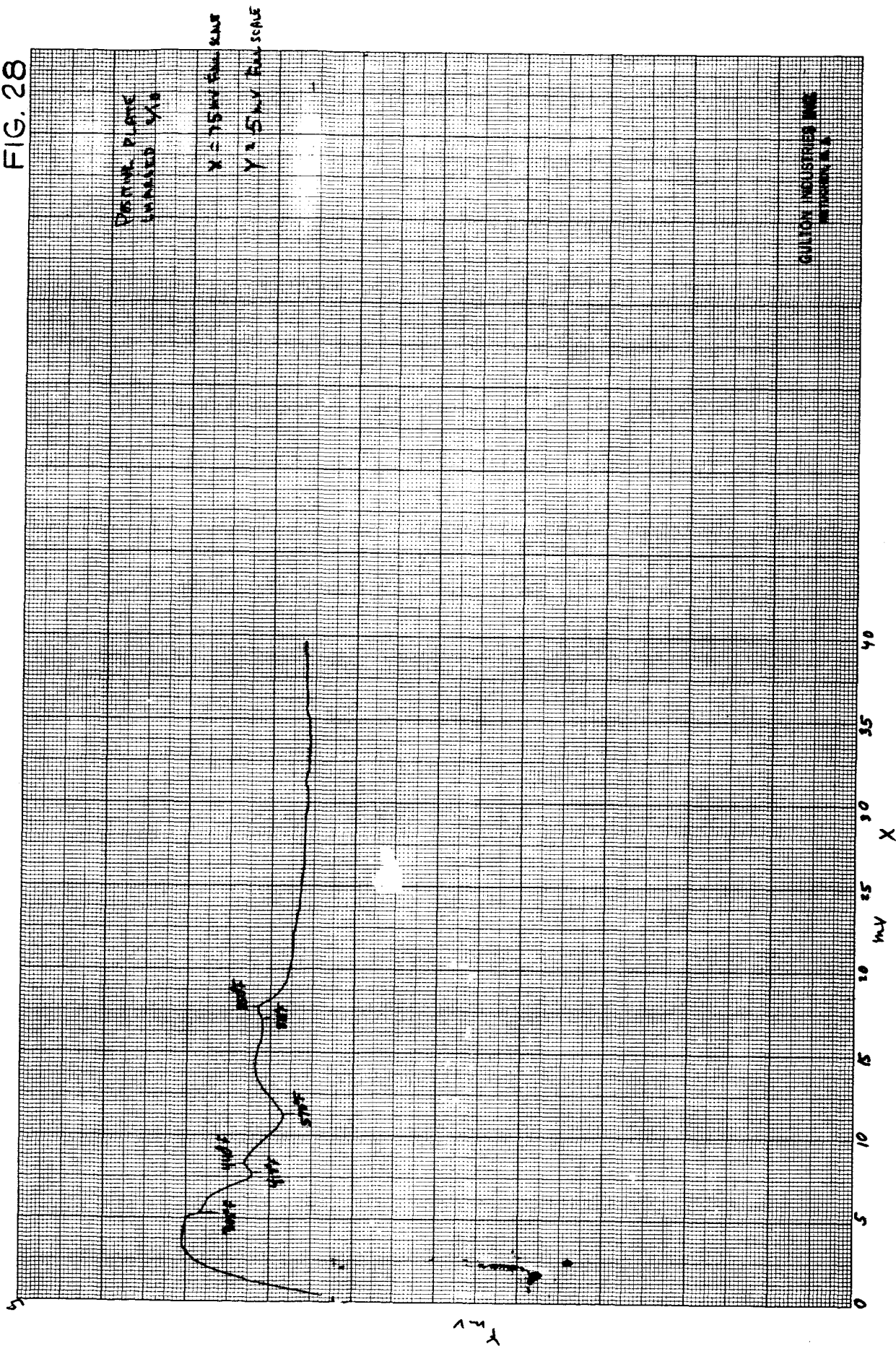


FIG. 29

DISCHARGED
NEGATIVE PLATE
 $V = 75 \text{ kV full}$
 $V = 5 \text{ kV full}$

5000 P

0 5 10 15 20 25 30 35 40
kV X

GULSON INDUSTRIES INC.
METHUEN, N. H.

DISCHARGED

Positive Value

SECRET

2705 TUD. AHS 2X

BULTON INDUSTRIES INC.
WEST GOSHEN, N.Y.

FIG. 30

